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On the Angular Momentum of Light

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Submitted in fulfillment of the requirements for the degree of Doctor of Philosophy

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Declaration

The research described in this thesis is my own, except where otherwise stated.

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Abstract

The idea is now well established that light possesses angular momentum and that this comes in two distinct forms, namely spin and orbital angular momentum which are associated with circular polarisation and helical phase fronts respectively. In this thesis, we explain that this is, in fact, a mere glimpse of a much larger picture: light possesses an *infinite* number of distinct angular momenta, the conservation of which in the strict absence of charge reflects the myriad rotational symmetries then inherent to Maxwell's equations. We recognise, moreover, that many of these angular momenta can be identified explicitly in light-matter interactions, which leads us in particular to identify new possibilities for the use of light to probe and manipulate chiral molecules.

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This was the most difficult part of my thesis to write: whenever I think I'm done, I find that I've left some people out!

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Publications

1. R. P. Cameron, S. M. Barnett and A. M. Yao. Optical helicity, optical spin and related quantities in electromagnetic theory. *New Journal of Physics*, 14:053050, 2012.
2. S. M. Barnett, R. P. Cameron and A. M. Yao. Duplex symmetry and its relation to the conservation of optical helicity. *Physical Review A* 86:013845, 2012.
3. R. P. Cameron and S. M. Barnett. Electric-magnetic symmetry and Noether's theorem. *New Journal of Physics* 14:123019, 2012.
4. R. P. Cameron. On the 'second potential' in electrodynamics. *Journal of Optics* 16:015708, 2013.
5. R. P. Cameron, S. M. Barnett and A. M. Yao. Discriminatory optical force for chiral molecules. *New Journal of Physics* 16:013020, 2014.
6. R. P. Cameron, S. M. Barnett and A. M. Yao. Optical helicity of interfering waves. *Journal of Modern Optics* 61:25-31, 2014.
7. R. P. Cameron, A. M. Yao and S. M. Barnett. Diffraction gratings for chiral molecules and their applications. *Journal of Physical Chemistry A* 118:3472-3478, 2014.
8. R. P. Cameron and S. M. Barnett. Optical activity in the scattering of structured light. *Physical Chemistry Chemical Physics* 16:25819-25829, 2014.
9. R. P. Cameron, F. C. Speirits, C. R. Gilson, L. Allen and S. M. Barnett. The azimuthal component of Poynting's vector and the angular momentum of light. *To be submitted*, 2014.

Summary

The original research described in this thesis spans a collection of topics in the theory of electrodynamics, each of which touches upon the angular momentum of light. Our interest lies primarily in the classical domain, although on occasion we delve into the quantum and semiclassical domains. The structure and content of the thesis may be summarised as follows.

In §1, we review certain well established results in the theory of electrodynamics. These have been chosen so as to make the thesis essentially self contained and should therefore be sufficient to understand the discussions that follow in §2-§5.

In §2, we make some rather formal observations about the theory of electrodynamics that underpin much of what follows in §3-§5. We begin by considering Maxwell's equations as written in the strict absence of charge and recall that these place the electric field \mathbf{E} and the magnetic flux density \mathbf{B} on equal footing, which permits the introduction, in addition to the familiar 'first potential' \mathbf{A}^\perp , of a 'second potential' \mathbf{C}^\perp . This leads us to observe in turn that the equations exhibit a remarkable *self-similarity* as one considers various integrals (such as \mathbf{A}^\perp and \mathbf{C}^\perp) of \mathbf{E} and \mathbf{B} , as well as various derivatives of \mathbf{E} and \mathbf{B} . Finally, we allow for the presence of electric charge and generalise some of our observations. In particular, we introduce and examine a seemingly reasonable general definition of \mathbf{C}^\perp ; a non-trivial problem, owing to the breakdown of electric-magnetic discrimination that accompanies the charge.

In §3, we turn our attention to the angular momentum of light and its fundamental description in the theory of electrodynamics. Again, we begin by considering light that is propagating freely in the strict absence of charge. The fact is well established that such light possesses rotation angular momentum

$$\mathcal{J} = \iiint_{\infty} \mathbf{r} \times (\mathbf{E} \times \mathbf{B}) \, d^3\mathbf{r}$$

and boost angular momentum

$$\mathcal{K} = \iiint_{\infty} \left[t \mathbf{E} \times \mathbf{B} - \frac{1}{2} \mathbf{r} (\mathbf{E} \cdot \mathbf{E} + \mathbf{B} \cdot \mathbf{B}) \right] d^3\mathbf{r}$$

and that the conservation of the rotation angular momentum \mathcal{J} is associated with circular rotations in space whereas the conservation of the boost angular momentum \mathcal{K} is associated with boosts, which can be regarded as hyperbolic rotations in spacetime. It is known, moreover, that the rotation angular momentum \mathcal{J} can itself be separated into independently conserved parts \mathcal{S} and \mathcal{L} that resemble what we might expect of spin and orbital angular momentum¹. It has been shown, however, that the operators $\hat{\mathcal{S}}$ and $\hat{\mathcal{L}}$ representing the spin \mathcal{S} and orbital angular momentum \mathcal{L} do *not* obey the usual angular momentum commutation relations, which has cast doubt upon their physical significance, although each is, nevertheless, associated with a rotational symmetry.

¹An analogous separation for the boost angular momentum \mathcal{K} yields a vanishing boost spin candidate and a non-vanishing boost orbital angular momentum candidate which thus comprises the totality of the boost angular momentum.

This controversial result, taken together with a simple idea familiar from particle physics, leads us to discover that light in fact possesses an *infinite* number of distinct angular momenta, which we recognise as being such because they have the dimensions of an angular momentum and are conserved. Spin and orbital angular momentum are but two of these. We attempt to elucidate the physical significance of the angular momenta and their conservation, as well as the similarities, relationships and distinctions between them, through various analogies and explicit examples. Moreover, we disambiguate the angular momenta from related but distinct properties of light such as the zilch $Z^{\alpha\beta}$, the conservation of which we interpret as being a reflection of the self-similarity that we unearthed in §2. Finally, we allow for the presence of charge and generalise some of our observations, finding in particular that the definition of C^\perp in the presence of charge that we proposed in §2 is indeed a reasonable one.

In §4, we introduce a variational description of freely propagating light that places \mathbf{E} and \mathbf{B} on equal footing, much in the spirit of §2. We use this description, together with Noether's theorem, to study symmetries and the conservation laws with which they are associated. This yields, in particular, a more fundamental perspective on the angular momenta discovered in §3: the conservation of the angular momenta, which are infinite in number, reflects the existence of an infinite number of ways in which it is possible to rotate freely propagating light. Additional hierarchies of symmetries and associated conservation laws, amongst them the conservation of $Z^{\alpha\beta}$, are also identified and attributed again to the self-similarity that we unearthed in §2.

In §5, we identify applications centred upon some of the angular momenta discovered in §3. Specifically, we observe that many optical activity phenomena: light-matter interactions in which left- and right-handed circular polarisations are distinguished, can be related explicitly to helicity, spin, etc. This is unsurprising, perhaps, given that these angular momenta differ in value for left- and right-handed circularly polarised light. We employ this new insight in the consideration of a well-established manifestation of optical activity (optical rotation), a dormant manifestation of optical activity (differential scattering) and a new manifestation of optical activity (discriminatory optical force for chiral molecules). The latter two may be developed into powerful new techniques for the probing and manipulation of chiral molecules.

We conclude in §6 by outlining possibilities for future research into chirality and optical activity which follow on from the research presented in §5.

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Chapter 1

Supporting Theory

1.1 Introduction

Electrodynamics; a word coined by Ampère [1], is concerned with (electrically)¹ charged matter, the electromagnetic field and their mutual interaction. It is understood, at present, that the electromagnetic interaction is responsible for *all* phenomena not attributable instead to the gravitational interaction, the strong interaction or the weak interaction² [8]; from the structure and properties of molecules and atoms which comprise the material world around us to the light radiated by the stars in the night sky [2, 3, 9–14].

The original research described in this thesis spans a collection of topics in the theory of electrodynamics, each of which touches upon the angular momentum of light. We begin in the present chapter by summarising the well established results that support the discussions in §2-§5.

Throughout, we imagine ourselves to be in an inertial frame of reference with time t and a right-handed Cartesian coordinate system: x, y and z , unless otherwise stated. Complex quantities are indicated as such using a tilde, with complex conjugation indicated using an asterisk. Quantum operators are indicated as such using a circumflex, with Hermitian conjugation indicated using a dagger. Unit vectors are indicated as such using a double circumflex. In the present chapter, as well as §2-§4, we adopt a modified version of the international system of units in which the electric constant ϵ_0 , the magnetic constant μ_0 and hence the speed of light in vacuum $c = 1/\sqrt{\epsilon_0\mu_0}$ are equal to unity. In §1.4 and §5, we revert, however, to the international system of units as it is usually recognised.

1.2 Classical electrodynamics

In §2-§5, we work within the classical domain, unless otherwise stated. In the present section, we therefore summarise some well established results from the theory of classical electrodynamics [2, 3, 9–11, 14].

¹Magnetically charged matter is occasionally considered in theory [2–7], although, at the time of writing, it has not been observed in experiment.

²The electromagnetic and weak interactions themselves comprise a unified electroweak interaction [8]. In this thesis, we neglect the influence of the weak interaction.

1.2.1 The microscopic equations

Consider N point particles of charge q_n , mass³ m_n and position $\mathbf{r}_n = \mathbf{r}_n(t)$ ($n = 1, \dots, N$) which give rise to a microscopic charge density $\rho = \rho(\mathbf{r}, t)$ and a microscopic current density $\mathbf{J} = \mathbf{J}(\mathbf{r}, t)$ as

$$\rho = \sum_{n=1}^N q_n \delta^3(\mathbf{r} - \mathbf{r}_n), \quad (1.1)$$

$$\mathbf{J} = \sum_{n=1}^N q_n \dot{\mathbf{r}}_n \delta^3(\mathbf{r} - \mathbf{r}_n), \quad (1.2)$$

with $\mathbf{r} = x\hat{\mathbf{x}} + y\hat{\mathbf{y}} + z\hat{\mathbf{z}}$ the position vector with $\hat{\mathbf{x}}$, $\hat{\mathbf{y}}$ and $\hat{\mathbf{z}}$ unit vectors in the $+x$, $+y$ and $+z$ directions, $\delta^3(\mathbf{r})$ a three-dimensional Dirac delta function and an overdot, notation due to Newton [15], indicating a derivative with respect to time t . The trajectory of the n th particle is governed by the Newton-Einstein-Lorentz equation [16, 17]:

$$\frac{d}{dt} \left(\frac{m_n \dot{\mathbf{r}}_n}{\sqrt{1 - |\dot{\mathbf{r}}_n|^2}} \right) = q_n [\mathbf{E}(\mathbf{r}_n, t) + \dot{\mathbf{r}}_n \times \mathbf{B}(\mathbf{r}_n, t)], \quad (1.3)$$

whilst the microscopic electric field $\mathbf{E} = \mathbf{E}(\mathbf{r}, t)$ and the microscopic magnetic flux density $\mathbf{B} = \mathbf{B}(\mathbf{r}, t)$ are governed by Maxwell's equations [17, 18]:

$$\nabla \cdot \mathbf{E} = \rho, \quad (1.4)$$

$$\nabla \cdot \mathbf{B} = 0, \quad (1.5)$$

$$\nabla \times \mathbf{E} = -\dot{\mathbf{B}}, \quad (1.6)$$

$$\nabla \times \mathbf{B} = \mathbf{J} + \dot{\mathbf{E}}, \quad (1.7)$$

with ∇ the gradient operator with respect to \mathbf{r} . (1.4) is Gauss's law, (1.5) is the analogue of Gauss's law for magnetism, (1.6) is the Faraday-Lenz law and (1.7) is Ampère's law as corrected by Maxwell [18], all in differential form, of course [2, 3, 9–11].

These equations (1.1)-(1.7) constitute an essentially complete statement of the theory of classical electrodynamics. Solving them requires finding the \mathbf{r}_n , \mathbf{E} and \mathbf{B} .

1.2.2 Scalar and magnetic vector potentials

Gauss's law for magnetism (1.5) and the Faraday-Lenz law (1.6) do not depend explicitly upon the particles and may be viewed, therefore, as geometrical identities obeyed by \mathbf{E} and \mathbf{B} . They can be solved by taking

$$\mathbf{E} = -\nabla\Phi - \dot{\mathbf{A}}, \quad (1.8)$$

$$\mathbf{B} = \nabla \times \mathbf{A}, \quad (1.9)$$

³More precisely, m_n is the bare rest mass of the n th particle [11].

for any scalar potential⁴ $\Phi = \Phi(\mathbf{r}, t)$ and magnetic vector potential $\mathbf{A} = \mathbf{A}(\mathbf{r}, t)$. To be consistent with the Newton-Einstein-Lorentz equation (1.3), Gauss's law (1.4) and the Ampère-Mawell law (1.7), we then require that

$$\frac{d}{dt} \left(\frac{m_n \dot{\mathbf{r}}_n}{\sqrt{1 - |\dot{\mathbf{r}}_n|^2}} \right) = q_n \left\{ -\nabla \Phi(\mathbf{r}_n, t) - \dot{\mathbf{A}}(\mathbf{r}_n, t) + \dot{\mathbf{r}}_n \times [\nabla \times \mathbf{A}(\mathbf{r}_n, t)] \right\}, \quad (1.10)$$

$$-\nabla^2 \Phi - \nabla \cdot \dot{\mathbf{A}} = \rho, \quad (1.11)$$

$$-\nabla^2 \mathbf{A} + \nabla (\nabla \cdot \mathbf{A}) = \mathbf{J} - \nabla \dot{\Phi} - \ddot{\mathbf{A}}, \quad (1.12)$$

with $\nabla^2 = \nabla \cdot \nabla$ the Laplacian operator with respect to \mathbf{r} . In moving our focus from the six quantities that are the components of \mathbf{E} and \mathbf{B} to the four quantities that are Φ and the components of \mathbf{A} , we must pay the price of going from three equations (1.3) that are *zeroth* order in temporal and spatial derivatives and eight equations (1.4)-(1.7) that are *first* order, to three equations (1.10) that are instead *first* order and four equations (1.11)-(1.12) that are instead *second* order.

Φ and \mathbf{A} are not uniquely defined in that \mathbf{E} and \mathbf{B} are unchanged by the transformation [19]

$$\begin{aligned} \Phi &\rightarrow \Phi + \dot{\chi} \\ \mathbf{A} &\rightarrow \mathbf{A} - \nabla \chi, \end{aligned} \quad (1.13)$$

for any time-odd Lorentz scalar field $\chi = \chi(\mathbf{r}, t)$; a so-called gauge function [2, 3, 9–11]. This freedom permits us to ‘choose a gauge’, by imposing a condition upon $\nabla \cdot \mathbf{A}$. The Coulomb gauge⁵:

$$\nabla \cdot \mathbf{A} = 0, \quad (1.14)$$

and a Lorenz gauge⁶ [20]:

$$\nabla \cdot \mathbf{A} + \dot{\Phi} = 0, \quad (1.15)$$

are but two examples of gauge choices.

1.2.3 Special relativity

In the theory of special relativity [2, 3, 10, 16, 21], the time $t = x^0$ and spatial coordinates $x = x^1$, $y = x^2$ and $z = x^3$ with which we have chosen to describe events are recognised as being the components of the position four vector $x^\alpha = (t, \mathbf{r})$. Raised indices taken from the start of the Greek alphabet (α, β, \dots), including α here, are referred to as being contravariant and can take on the values 0, corresponding to time, and 1, 2 and 3, corresponding to space. Letters taken from the start of the Roman alphabet (a, b, \dots), when employed as contravariant indices, may assume the values 1, 2 and 3 corresponding to space only.

⁴From here onwards, it is to be understood where relevant that quantities are ‘microscopic’, unless otherwise stated.

⁵The Coulomb gauge condition can be seen in Maxwell's original work [18].

⁶There are, in fact, many Lorenz gauges, for a so-called restricted gauge transformation, with $\nabla^2 \chi - \ddot{\chi} = 0$, maintains the equality seen in (1.15) [2].

The principle of special relativity, due to Einstein [16], tells us in particular that the laws of physics, whilst holding in the x^α coordinate system, should also hold in all other coordinate systems $x^{\alpha'} = (t', \mathbf{r}')$ related to x^α as

$$x^{\alpha'} = \Lambda_{\alpha}^{\alpha'} x^{\alpha}, \quad (1.16)$$

with the array of constants $\Lambda_{\alpha}^{\alpha'}$ describing (proper) rotations and / or boosts and where we have introduced the summation convention, also due to Einstein [22]: here and in what follows, it is to be understood that a double appearance of an index implies summation over its allowed values. For $x^{\alpha'}$ rotated relative to x^α about the $+z$ axis through an angle θ in the usual sense, given by the right-hand rule;

$$\Lambda_{\alpha}^{\alpha'} = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & \cos \theta & \sin \theta & 0 \\ 0 & -\sin \theta & \cos \theta & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix}, \quad (1.17)$$

whereas for a boost in standard configuration of $x^{\alpha'}$ relative to x^α in the $+z$ direction with speed v and associated rapidity $\phi = \arctan v$;

$$\Lambda_{\alpha}^{\alpha'} = \begin{pmatrix} \cosh \phi & -\sinh \phi & 0 & 0 \\ -\sinh \phi & \cosh \phi & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix}, \quad (1.18)$$

to give but two explicit examples [2, 3, 10, 14, 21]. Reciprocally,

$$x^{\alpha} = \Lambda_{\alpha'}^{\alpha} x^{\alpha'} \quad (1.19)$$

with the array $\Lambda_{\alpha'}^{\alpha}$ being the inverse of $\Lambda_{\alpha}^{\alpha'}$, of course. More generally, an object with components described by r ($r = 0, 1, \dots$) raised indices, the values $X^{\alpha'\beta'\dots\omega'}$ of which in $x^{\alpha'}$ are related to those $X^{\alpha\beta\dots\omega}$ in x^α as

$$X^{\alpha'\beta'\dots\omega'} = \Lambda_{\alpha}^{\alpha'} \Lambda_{\beta}^{\beta'} \dots \Lambda_{\omega}^{\omega'} X^{\alpha\beta\dots\omega}, \quad (1.20)$$

is said to be a contravariant tensor of rank r .

The partial derivatives $\partial_t = \partial_0$, $\partial_x = \partial_1$, $\partial_y = \partial_2$ and $\partial_z = \partial_3$ are recognised as being the components of the partial derivative four vector $\partial_{\alpha} = (\partial_t, \nabla)$. Lowered indices taken from the start of the Greek alphabet, including α here, are referred to as being covariant and, like contravariant indices, can also take on the values 0, corresponding to time, and 1, 2 and 3, corresponding to space. Letters taken from the start of the Roman alphabet, when employed as covariant indices, may assume the values 1, 2 and 3 corresponding to space only. The components $\partial_{\alpha'} = (\partial_{t'}, \nabla')$ of the partial derivative four vector in $x^{\alpha'} = (t', \mathbf{r}')$ are related to those ∂_{α} in x^α as

$$\partial_{\alpha'} = \Lambda_{\alpha'}^{\alpha} \partial_{\alpha}. \quad (1.21)$$

More generally, an object with components described by r ($r = 0, 1, \dots$) lowered indices, the values $X_{\alpha'\beta'\dots\omega'}$ of which in $x^{\alpha'}$ are related to those $X_{\alpha\beta\dots\omega}$ in x^α as

$$X_{\alpha'\beta'\dots\omega'} = \Lambda_{\alpha'}^\alpha \Lambda_{\beta'}^\beta \dots \Lambda_{\omega'}^\omega X_{\alpha\beta\dots\omega}, \quad (1.22)$$

is said to be a covariant tensor of rank r .

We now introduce the Minkowski metric tensor $\eta_{\alpha\beta} = \eta^{\alpha\beta} = \text{diag}(1, -1, -1, -1)$ which plays a dual role in that it defines the spacetime interval $d\tau$ between events at x^α and $x^\alpha + dx^\alpha$ as

$$d\tau^2 = \eta_{\alpha\beta} dx^\alpha dx^\beta \quad (1.23)$$

and can be used to interconvert contravariant and covariant indices as

$$\eta_{\alpha\beta} X^\beta = X_\alpha, \quad (1.24)$$

$$X^\alpha = \eta^{\alpha\beta} X_\beta, \quad (1.25)$$

for example [2, 21]. Thus, we can have so-called mixed tensors, which possess both contravariant and covariant indices, an example of which is the Kronecker delta tensor $\delta_\beta^\alpha = \text{diag}(1, 1, 1, 1)$. Finally, let us introduce the Levi-Civita pseudotensor⁷ $\epsilon^{\alpha\beta\gamma\delta}$, defined as $\epsilon^{0123} = 1$ whilst alternating in sign under exchange of any two of these indices and having the remainder of its components vanish [2, 10, 21].

The significance of this formalism lies in the fact that an equation that holds in x^α and is expressible in terms of tensors and pseudotensors manifestly holds with the same form in $x^{\alpha'}$ [21]. This is true in particular of the results presented in §1.2.1 and §1.2.2. To demonstrate this, let us introduce the position four vector $x_n^\alpha = (t, \mathbf{r}_n)$ of the n th particle, the linear-momentum moment four vector $p_n^\alpha = m_n (1, \dot{\mathbf{r}}_n) / \sqrt{1 - |\dot{\mathbf{r}}_n|^2}$ of the n th particle, the current four vector $J^\alpha = (\rho, \mathbf{J})$ and a magnetic potential four vector $A^\alpha = (\Phi, \mathbf{A})$. The electromagnetic field tensor $F^{\alpha\beta}$ and the dual electromagnetic field pseudotensor $G^{\alpha\beta}$ are defined in turn as

$$F_{\alpha\beta} = \partial_\alpha A_\beta - \partial_\beta A_\alpha, \quad (1.26)$$

$$G^{\alpha\beta} = \epsilon^{\alpha\beta\gamma\delta} F_{\gamma\delta} / 2. \quad (1.27)$$

In matrix form

$$F^{\alpha\beta} = \begin{pmatrix} 0 & -E_x & -E_y & -E_z \\ E_x & 0 & -B_z & B_y \\ E_y & B_z & 0 & -B_x \\ E_z & -B_y & B_x & 0 \end{pmatrix} \quad (1.28)$$

⁷As we have restricted our attention here to the proper (and homogeneous) transformations (1.20) and (1.22), the distinction between tensors and pseudotensors is of no consequence. The distinction *is* important, however, if we allow for improper transformations, specifically with inversions of spatial coordinates [2, 10].

and

$$G^{\alpha\beta} = \begin{pmatrix} 0 & -B_x & -B_y & -B_z \\ B_x & 0 & E_z & -E_y \\ B_y & -E_z & 0 & E_x \\ B_z & E_y & -E_x & 0 \end{pmatrix}. \quad (1.29)$$

We have then that

$$dp_n^\alpha/d\tau_n = q_n F^{\beta\alpha}(x_n) dx_{n\beta}/d\tau_n, \quad (1.30)$$

$$\partial_\beta F^{\alpha\beta} = -J^\alpha, \quad (1.31)$$

$$\partial_\beta G^{\alpha\beta} = 0, \quad (1.32)$$

with $d\tau_n = \sqrt{1 - |\dot{\mathbf{r}}_n|^2} dt$ a proper time interval for the n th particle. For $\alpha = 0$, (1.30) describes the rate of change of energy of the n th particle and for $\alpha = 1, 2$ and 3 yields the x, y and z components of the Newon-Einstein-Lorentz force law (1.3). For $\alpha = 0$, (1.31) is Gauss's law (1.4) and for $\alpha = 1, 2$ and 3 yields the x, y and z components of the Ampère-Maxwell law (1.7). For $\alpha = 0$, (1.32) is Gauss's law for magnetism (1.5) and for $\alpha = 1, 2, 3$ yields the x, y, z components of the Faraday-Lenz law (1.6). Thus, the classical theory of electrodynamics manifestly respects the principle of special relativity, as claimed [2, 3, 10, 14, 21].

On occasion, we will find it useful to consider x^α together with coordinate systems $x^{\alpha'}$ related to x^α as above but with boosts *excluded*. Quantities that transform analogously to \mathbf{r} in this restricted three-dimensional sense are referred to as being *rotational* tensors and *rotational* pseudotensors [2]. Vectors and pseudovectors are thus rotational tensors and rotational pseudotensors of rank one. We label the components of rotational tensors and pseudotensors using indices taken from the start of the Roman alphabet in parenthesis. These may assume the values 1, 2 and 3 corresponding to space only and we make no distinction between raised and lowered forms, taking

$$A^1 = -A_1 = A^{(1)} = A_{(1)} = A_x, \quad (1.33)$$

$$A^a A_a = -A_{(a)} A_{(a)} = -A^{(a)} A_{(a)} = -A^{(a)} A^{(a)} = -A_x^2 - A_y^2 - A_z^2, \quad (1.34)$$

for example. Of particular use to us is the Kronecker delta rotational tensor $\delta_{(ab)} = \text{diag}(1, 1, 1)$ and the Levi-Civita rotational pseudotensor $\epsilon_{(abc)}$, defined as $\epsilon_{(123)} = 1$ whilst alternating in sign under exchange of any two of these indices and having the remainder of its components vanish.

1.2.4 Conservation laws

It is required by Gauss's law (1.4) and the Ampère-Maxwell law (1.7) and indeed follows from the definitions seen in (1.1) and (1.2) that

$$\dot{\rho} + \nabla \cdot \mathbf{J} = 0. \quad (1.35)$$

The significance of (1.35) may be seen by integrating both sides over a finite volume V with bounding surface S and making use of Gauss's integral theorem [3], thus obtaining

$$\frac{d}{dt} \iiint_V \rho d^3\mathbf{r} = - \iint_S \mathbf{J} \cdot d^2\mathbf{r}, \quad (1.36)$$

which tells us that changes in t of the charge $\iiint_V \rho d^3\mathbf{r}$ contained in V are compensated for by an equal and opposite flux $\iint_S \mathbf{J} \cdot d^2\mathbf{r}$ of charge through S . Hence, (1.35) is said to be a continuity equation for charge and its integral solution (1.36) is said to be a local conservation law for charge. If V now extends over all space, (1.36) becomes

$$\begin{aligned} \frac{d}{dt} \iiint_{\infty} \rho d^3\mathbf{r} &= \frac{dQ}{dt} \\ &= 0, \end{aligned} \quad (1.37)$$

with $Q = \sum_{n=1}^N q_n$ the total charge of the particles. This (1.37) is said to be a global conservation law for charge.

Such mathematical arguments are independent of the physical nature of charge and it is clear, therefore, that any equation of the form seen in (1.35) embodies the local and hence global conservation of a quantity. It will be noticed that (1.35) is $\partial_\alpha J^\alpha = 0$. We should be clear, however, that the principle of special relativity does not require a continuity equation to be expressible in terms of tensors and / or pseudotensors, in general.

1.2.5 Solenoidal and irrotational pieces, reciprocal space and the normal variables

The observation is attributed to Helmholtz [23] that a vector field or pseudovector field $\mathbf{V} = \mathbf{V}(\mathbf{r}, t)$ can be separated into a *solenoidal* piece \mathbf{V}^\perp and an *irrotational* piece \mathbf{V}^\parallel as

$$\mathbf{V} = \mathbf{V}^\perp + \mathbf{V}^\parallel, \quad (1.38)$$

with $\nabla \cdot \mathbf{V}^\perp = 0$ and $\nabla \times \mathbf{V}^\parallel = 0$, by definition [2, 3, 11, 12]. The significance of such separations is clearer, perhaps, in reciprocal rather than ordinary space. To illustrate this, let us introduce in a general manner the spatial Fourier transform $\tilde{Y} = \tilde{Y}(\mathbf{k}, t)$ of a real field $Y = Y(\mathbf{r}, t)$ in ordinary space as [11]

$$\tilde{Y} = \iiint_{\infty} \frac{1}{2\sqrt{2\pi^3}} Y \exp(-i\mathbf{k} \cdot \mathbf{r}) d^3\mathbf{r}, \quad (1.39)$$

with \mathbf{k} a wavevector. It is then found that the spatial Fourier transforms $\tilde{\mathbf{V}}^\perp$ and $\tilde{\mathbf{V}}^\parallel$ of \mathbf{V}^\perp and \mathbf{V}^\parallel satisfy $\mathbf{k} \cdot \tilde{\mathbf{V}}^\perp = 0$ and $\mathbf{k} \times \tilde{\mathbf{V}}^\parallel = 0$ and are thus everywhere perpendicular and parallel to \mathbf{k} in reciprocal space. For this reason, $\tilde{\mathbf{V}}^\perp$ and $\tilde{\mathbf{V}}^\parallel$ are sometimes referred to as the *transverse* and

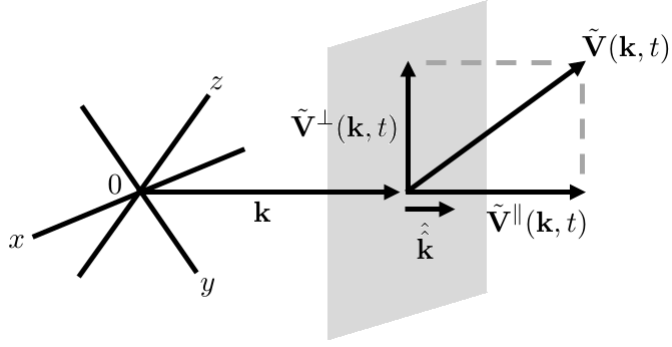


Figure 1.1: The spatial Fourier transform $\tilde{\mathbf{V}}(\mathbf{k}, t)$ of a vector or pseudovector field $\mathbf{V}(\mathbf{r}, t)$ can be separated into a transverse piece $\tilde{\mathbf{V}}^\perp(\mathbf{k}, t)$ and a longitudinal piece $\tilde{\mathbf{V}}^\parallel(\mathbf{k}, t)$, which are everywhere perpendicular and parallel to \mathbf{k} in reciprocal space, as depicted here. We have taken $\tilde{\mathbf{V}}(\mathbf{k}, t)$ to be real for the sake of illustration.

longitudinal pieces of the spatial Fourier transform $\tilde{\mathbf{V}}$ of \mathbf{V} [11, 12]: see figure 1.1. Thus,

$$\tilde{V}_{(a)}^\perp = \hat{k}_{(a)} \hat{k}_{(b)} \tilde{V}_{(b)}, \quad (1.40)$$

$$\tilde{V}_{(a)}^\parallel = \left[\delta_{(ab)} - \hat{k}_{(a)} \hat{k}_{(b)} \right] \tilde{V}_{(b)}, \quad (1.41)$$

from which it follows that

$$V_{(a)}^\perp = \int \int \int_{-\infty}^{\infty} \delta_{(ab)}^\perp(\mathbf{r} - \mathbf{r}') V_{(b)}(\mathbf{r}') d^3\mathbf{r}', \quad (1.42)$$

$$V_{(a)}^\parallel = \int \int \int_{-\infty}^{\infty} \delta_{(ab)}^\parallel(\mathbf{r} - \mathbf{r}') V_{(b)}(\mathbf{r}') d^3\mathbf{r}', \quad (1.43)$$

with $\delta_{(ab)}^\perp(\mathbf{r})$ the so-called transverse delta function and $\delta_{(ab)}^\parallel(\mathbf{r})$ the so-called longitudinal delta function, given by [11, 12]

$$\delta_{(ab)}^\perp(\mathbf{r}) = \frac{2}{3} \delta_{(ab)} \delta^3(\mathbf{r}) - \frac{1}{4\pi|\mathbf{r}|^3} \left[\delta_{(ab)} - \hat{r}_{(a)} \hat{r}_{(b)} \right], \quad (1.44)$$

$$\delta_{(ab)}^\parallel(\mathbf{r}) = \frac{1}{3} \delta_{(ab)} \delta^3(\mathbf{r}) + \frac{1}{4\pi|\mathbf{r}|^3} \left[\delta_{(ab)} - \hat{r}_{(a)} \hat{r}_{(b)} \right]. \quad (1.45)$$

Such separations are not obviously expressible using the language of tensors and pseudotensors inherent to the theory of special relativity and there exists no simple relationship between \mathbf{V}^\perp and \mathbf{V}^\parallel and their counterparts in another coordinate system $x^{\alpha'}$, in general [11]. They nevertheless appear naturally in many contexts and yield important insights. Amongst these lies the fact that a gauge transformation (1.13) changes Φ and the irrotational piece \mathbf{A}^\parallel of \mathbf{A} whilst leaving the solenoidal piece \mathbf{A}^\perp of \mathbf{A} unchanged. Thus, it is Φ and \mathbf{A}^\parallel in particular that suffer the gauge freedom of the electromagnetic field whereas \mathbf{A}^\perp is, in fact, uniquely defined [11].

Of particular interest to us are the normal variables $\tilde{\alpha} = \tilde{\alpha}(\mathbf{k}, t)$ in reciprocal space which are

transverse ($\mathbf{k} \cdot \tilde{\alpha} = 0$) and governed by the equations⁸

$$\dot{\tilde{\alpha}} + i|\mathbf{k}|\tilde{\alpha} = \frac{i}{\sqrt{2|\mathbf{k}|}} \tilde{\mathbf{J}}^\perp. \quad (1.46)$$

The $\tilde{\alpha}$ evolve independently of each other in t when the spatial Fourier transform $\tilde{\mathbf{J}}^\perp$ of the solenoidal piece \mathbf{J}^\perp of \mathbf{J} vanishes ($\tilde{\mathbf{J}}^\perp = 0$). Their introduction can be traced back at least as far as the work of Darwin [24]. The solenoidal piece \mathbf{E}^\perp of \mathbf{E} , \mathbf{B} and \mathbf{A}^\perp are determined by the $\tilde{\alpha}$ as [11]

$$\mathbf{E}^\perp = \int \int \int_{-\infty}^{\infty} \frac{i}{4} \sqrt{\frac{|\mathbf{k}|}{\pi^3}} [\tilde{\alpha} \exp(i\mathbf{k} \cdot \mathbf{r}) - \tilde{\alpha}^* \exp(-i\mathbf{k} \cdot \mathbf{r})] d^3\mathbf{k}, \quad (1.47)$$

$$\mathbf{B} = \int \int \int_{-\infty}^{\infty} \frac{i}{4\sqrt{\pi^3|\mathbf{k}|}} \mathbf{k} \times [\tilde{\alpha} \exp(i\mathbf{k} \cdot \mathbf{r}) - \tilde{\alpha}^* \exp(-i\mathbf{k} \cdot \mathbf{r})] d^3\mathbf{k}, \quad (1.48)$$

$$\mathbf{A}^\perp = \int \int \int_{-\infty}^{\infty} \frac{1}{4\sqrt{\pi^3|\mathbf{k}|}} [\tilde{\alpha} \exp(i\mathbf{k} \cdot \mathbf{r}) + \tilde{\alpha}^* \exp(-i\mathbf{k} \cdot \mathbf{r})] d^3\mathbf{k}. \quad (1.49)$$

In contrast, the irrotational piece \mathbf{E}^\parallel of \mathbf{E} is determined by the \mathbf{r}_n as [11]

$$\begin{aligned} \mathbf{E}^\parallel &= \int \int \int_{-\infty}^{\infty} \frac{\rho(\mathbf{r}', t) (\mathbf{r} - \mathbf{r}')}{4\pi |\mathbf{r} - \mathbf{r}'|^3} d^3\mathbf{r}' \\ &= \sum_{n=1}^N \frac{q_n (\mathbf{r} - \mathbf{r}_n)}{4\pi |\mathbf{r} - \mathbf{r}_n|^3}, \end{aligned} \quad (1.50)$$

this being the non-retarded⁹ Coulomb field of the particles. Thus, the dynamical degrees of freedom of the electromagnetic field are embodied by the $\tilde{\alpha}$ and are exhibited by \mathbf{E}^\perp and \mathbf{B} , which we refer to collectively as the radiation field [11–13]. Of course, (1.46) must be solved simultaneously with the Newton-Einstein-Lorentz equation (1.3), in general. Knowledge of the $\tilde{\alpha}$ together with the \mathbf{r}_n then constitutes an essentially complete description of the system, one with minimal redundancy [11].

1.2.6 Partitioning ρ and \mathbf{J} and the transition to the macroscopic domain

It is often convenient to partition ρ and \mathbf{J} into pieces of distinct character. For a single molecule or atom, with some of the N particles being electrons whilst the remainder are nuclei, we take [11, 12]

$$\rho = \rho_f - \nabla \cdot \mathbf{P}, \quad (1.51)$$

$$\mathbf{J} = \mathbf{J}_f + \dot{\mathbf{P}} + \nabla \times \mathbf{M} + \mathbf{J}_R, \quad (1.52)$$

⁸The $\tilde{\alpha}$ here are larger than those defined in the book by Cohen-Tannoudji, Dupont-Roc and Grynberg [11], for example, by a factor of $\sqrt{\hbar}$, with \hbar the reduced Planck constant.

⁹Like \mathbf{E}^\parallel , \mathbf{E}^\perp also exhibits non-retarded behaviour such that \mathbf{E} itself is retarded [11].

for

$$\rho_f = Q \delta^3(\mathbf{r} - \mathbf{R}), \quad (1.53)$$

$$\mathbf{P} = \sum_{n=1}^N q_n (\mathbf{r}_n - \mathbf{R}) \int_0^1 \delta^3[\mathbf{r} - \mathbf{R} - u(\mathbf{r} - \mathbf{r}_n)] du, \quad (1.54)$$

$$\mathbf{J}_f = Q \dot{\mathbf{R}} \delta^3(\mathbf{r} - \mathbf{R}), \quad (1.55)$$

$$\mathbf{M} = \sum_{n=1}^N q_n (\mathbf{r}_n - \mathbf{R}) \times (\dot{\mathbf{r}}_n - \dot{\mathbf{R}}) \int_0^1 u \delta^3[\mathbf{r} - \mathbf{R} - u(\mathbf{r} - \mathbf{r}_n)] du, \quad (1.56)$$

$$\mathbf{J}_R = \nabla \times (\mathbf{P} \times \dot{\mathbf{R}}), \quad (1.57)$$

with $\mathbf{R} = \mathbf{R}(t)$ the position of a point in the vicinity of the particles that may coincide with the position of their centre of energy but need not necessarily. The free charge density ρ_f describes a single point charge Q located at \mathbf{R} . The components $P_{(a)}$ of the polarisation \mathbf{P} can be expanded as [11, 12]

$$P_{(a)} = \sum_{i=1}^{\infty} (-1)^{i+1} d_{(a a_2 \dots a_i)}^{(i)} \partial_{a_2} \dots \partial_{a_i} \delta^3(\mathbf{r} - \mathbf{R}), \quad (1.58)$$

with the components $d_{(a_1 a_2 \dots a_i)}^{(i)} = d_{(a_1 a_2 \dots a_i)}^{(i)}(t)$ of the i th ($i = 1, 2, \dots$) electric multipole moment of the molecule or atom's charge distribution¹⁰ defined here by us as being

$$d_{(a_1 a_2 \dots a_i)}^{(i)} = \sum_{n=1}^N \frac{q_n}{i!} (\mathbf{r}_n - \mathbf{R})_{(a_1)} (\mathbf{r}_n - \mathbf{R})_{(a_2)} \dots (\mathbf{r}_n - \mathbf{R})_{(a_i)}. \quad (1.59)$$

The free current density \mathbf{J}_f describes a single point charge Q located at \mathbf{R} moving with velocity $\dot{\mathbf{R}}$. The magnetisation \mathbf{M} can be expanded as [11, 12]

$$M_{(a)} = \sum_{i=1}^{\infty} (-1)^{i+1} m_{(a a_2 \dots a_i)}'^{(i)} \partial_{a_2} \dots \partial_{a_i} \delta^3(\mathbf{r} - \mathbf{R}), \quad (1.60)$$

with the components $m_{(a_1 a_2 \dots a_i)}'^{(i)} = m_{(a_1 a_2 \dots a_i)}'^{(i)}(t)$ of the i th ($i = 1, 2, \dots$) magnetic multipole moment of the molecule or atom's current distribution defined here by us as being

$$m_{(a_1 a_2 \dots a_i)}'^{(i)} = \sum_{n=1}^N \frac{q_n i}{(i+1)!} \left[(\mathbf{r}_n - \mathbf{R}) \times (\dot{\mathbf{r}}_n - \dot{\mathbf{R}}) \right]_{(a_1)} (\mathbf{r}_n - \mathbf{R})_{(a_2)} \dots (\mathbf{r}_n - \mathbf{R})_{(a_i)}. \quad (1.61)$$

The Röntgen current density \mathbf{J}_R describes a relativistic effect: should the molecule or atom possess a non-vanishing \mathbf{P} and be translating with non-vanishing velocity $\dot{\mathbf{R}}$, it will possess an apparent magnetisation of $\mathbf{P} \times \dot{\mathbf{R}}$ [12]. ρ_f and \mathbf{J}_f happen to vanish ($\rho_f = 0$, $\mathbf{J}_f = 0$) of course, owing to the electric neutrality ($Q = 0$) of the molecule or atom. They would be non-vanishing, however, for an ion [2, 3].

Introducing the electric displacement field $\mathbf{D} = \mathbf{D}(\mathbf{r}, t)$ and the magnetic field $\mathbf{H} = \mathbf{H}(\mathbf{r}, t)$ through

¹⁰Formally, Q is the zeroth electric multipole moment of the molecule or atom's charge distribution [25].

the constitutive relations [2, 3]

$$\mathbf{D} = \mathbf{E} + \mathbf{P}, \quad (1.62)$$

$$\mathbf{B} = \mathbf{H} + \mathbf{M}', \quad (1.63)$$

with $\mathbf{M}' = \mathbf{M} + \mathbf{P} \times \dot{\mathbf{R}}$ an effective magnetisation, we can rewrite Maxwell's equations (1.4)-(1.7) as

$$\nabla \cdot \mathbf{D} = \rho_f, \quad (1.64)$$

$$\nabla \cdot \mathbf{B} = 0, \quad (1.65)$$

$$\nabla \times \mathbf{E} = -\dot{\mathbf{B}}, \quad (1.66)$$

$$\nabla \times \mathbf{H} = \mathbf{J}_f + \dot{\mathbf{D}}. \quad (1.67)$$

These ideas may be extended readily to account for multiple molecules or atoms, in particular to describe a material medium. Contributions made to ρ and \mathbf{J} by particles not bound to a specific molecule or atom, such as the conduction electrons in a metal, are then incorporated additionally in ρ_f and \mathbf{J}_f . By performing an appropriate spatial averaging procedure on (1.64)-(1.67), the familiar *macroscopic* Maxwell equations which govern the propagation of light through the medium may then be recovered [2, 3].

1.2.7 Solutions

Solving equations (1.1)-(1.7) in a fully consistent manner for the \mathbf{r}_n , \mathbf{E} and \mathbf{B} turns out to be an intractable problem, in general. Exact solutions can be obtained, however, under certain restricted circumstances.

In the strict absence of charge, Maxwell's equations (1.4)-(1.7) reduce to

$$\nabla \cdot \mathbf{E} = 0, \quad (1.68)$$

$$\nabla \cdot \mathbf{B} = 0, \quad (1.69)$$

$$\nabla \times \mathbf{E} = -\dot{\mathbf{B}}, \quad (1.70)$$

$$\nabla \times \mathbf{B} = \dot{\mathbf{E}}, \quad (1.71)$$

which govern light that is propagating freely. The simplest solution to Maxwell's equations as written in the strict absence of charge (1.68)-(1.71) is, perhaps, a single plane wave, for which [2, 3, 25]

$$\mathbf{E} = \Re \left\{ \tilde{\mathbf{E}}_0 \exp [i (\mathbf{k} \cdot \mathbf{r} - \omega t)] \right\}, \quad (1.72)$$

$$\mathbf{B} = \Re \left\{ \hat{\mathbf{k}} \times \tilde{\mathbf{E}}_0 \exp [i (\mathbf{k} \cdot \mathbf{r} - \omega t)] \right\}, \quad (1.73)$$

with \Re a function that yields the real part of its argument, $\tilde{\mathbf{E}}_0$ a complex vector satisfying $\mathbf{k} \cdot \tilde{\mathbf{E}}_0 = 0$ and which dictates the amplitude and polarisation of the wave, \mathbf{k} the wavevector of the wave and $\omega = |\mathbf{k}|$ the angular frequency of the wave. For concreteness, let us consider propagation in the $+z$ direction so that $\tilde{\mathbf{E}}_0 = \tilde{E}_{0x} \hat{\mathbf{x}} + \tilde{E}_{0y} \hat{\mathbf{y}}$ and $\mathbf{k} = |\mathbf{k}| \hat{\mathbf{z}}$. Taking $\tilde{E}_{0x} = E_0$ and $\tilde{E}_{0y} = 0$ with $E_0 > 0$,

for example, then gives a wave of amplitude E_0 that is linearly polarised parallel to the x axis. For $\tilde{E}_{0x} = E_0$ and $\tilde{E}_{0y} = \pm iE_0$ with $E_0 > 0$ we have instead a circularly polarised wave of amplitude E_0 , where the upper and lower signs refer to left- and right-handed circular polarisations in the optics convention [2], which we adopt. A quantity of particular use for us is the polarisation parameter

$$\sigma = i\hat{\mathbf{k}} \cdot (\tilde{\mathbf{E}}_0 \times \tilde{\mathbf{E}}_0^*) / \tilde{\mathbf{E}}_0 \cdot \tilde{\mathbf{E}}_0^* \quad (1.74)$$

of the wave, which is $\sigma = 0$ for linear polarisation and $\sigma = \pm 1$ for left- and right-handed circular polarisations. We can construct other types of freely propagating light by *superposing* plane waves, in any manner we like. If we restrict our attention to superpositions that only involve plane waves of angular frequency ω , we then have in general that

$$\mathbf{E} = \Re \left[\tilde{\mathbf{E}} \exp(-i\omega t) \right], \quad (1.75)$$

$$\mathbf{B} = \Re \left[\tilde{\mathbf{B}} \exp(-i\omega t) \right], \quad (1.76)$$

with the complex quantities $\tilde{\mathbf{E}} = \tilde{\mathbf{E}}(\mathbf{r})$ and $\tilde{\mathbf{B}} = \tilde{\mathbf{B}}(\mathbf{r})$ satisfying

$$\nabla \cdot \tilde{\mathbf{E}} = 0, \quad (1.77)$$

$$\nabla \cdot \tilde{\mathbf{B}} = 0, \quad (1.78)$$

$$\nabla \times \tilde{\mathbf{E}} = i\omega \tilde{\mathbf{B}}, \quad (1.79)$$

$$\nabla \times \tilde{\mathbf{B}} = -i\omega \tilde{\mathbf{E}}. \quad (1.80)$$

An interesting example of such freely propagating monochromatic light is a so-called Bessel beam, which is most conveniently described in terms of scalar Φ and magnetic \mathbf{A} potentials in the Lorenz gauge (1.15) as

$$\Phi = \Re \left[\tilde{\Phi} \exp(-i\omega t) \right], \quad (1.81)$$

$$\mathbf{A} = \Re \left[\tilde{\mathbf{A}} \exp(-i\omega t) \right], \quad (1.82)$$

with the complex quantities $\tilde{\Phi} = \tilde{\Phi}(\mathbf{r})$ and $\tilde{\mathbf{A}} = \tilde{\mathbf{A}}(\mathbf{r})$ given, for propagation in the $+z$ direction, by

$$\tilde{\Phi} = \nabla \cdot \tilde{\mathbf{A}} / i\omega, \quad (1.83)$$

$$\tilde{\mathbf{A}} = \tilde{\mathbf{A}}_0 J_\ell(\kappa s) \exp(i\ell\phi) \exp(ik_z z), \quad (1.84)$$

in cylindrical coordinates s, ϕ and z , with $\tilde{\mathbf{A}}_0$ a complex vector satisfying $\hat{\mathbf{z}} \cdot \tilde{\mathbf{A}}_0 = 0$ and which dictates the amplitude and polarisation of the wave, $J_\ell(\kappa s)$ is a Bessel function of order $\ell \in \{0, \pm 1, \dots\}$ and $\omega = \sqrt{\kappa^2 + k_z^2}$ [26]. For $\ell \neq 0$, this light has a line of perfect darkness at $z = 0$: a vortex, about which the phase fronts of the light twist helically with winding number ℓ . When considering monochromatic light, it is appropriate in some practical calculations to average quantities in t over a single period $2\pi/\omega$ of oscillation. We denote such cycle-averaging with an overbar.

Another tractable problem of interest to us occurs when particles are present, but their motion is

fixed so that ρ and \mathbf{J} are known a priori. Maxwell's equations (1.11) and (1.12) can then be solved rather elegantly again by adopting the Lorenz gauge (1.15), wherein [2, 3, 20]

$$\Phi = \iiint_{\infty} \frac{\rho(\mathbf{r}', t - |\mathbf{r} - \mathbf{r}'|)}{4\pi|\mathbf{r} - \mathbf{r}'|} d^3\mathbf{r}', \quad (1.85)$$

$$\mathbf{A} = \iiint_{\infty} \frac{\mathbf{J}(\mathbf{r}', t - |\mathbf{r} - \mathbf{r}'|)}{4\pi|\mathbf{r} - \mathbf{r}'|} d^3\mathbf{r}', \quad (1.86)$$

which are manifestly retarded. Thus,

$$\mathbf{E} = -\nabla \iiint_{\infty} \frac{\rho(\mathbf{r}', t - |\mathbf{r} - \mathbf{r}'|)}{4\pi|\mathbf{r} - \mathbf{r}'|} d^3\mathbf{r}' - \frac{\partial}{\partial t} \iiint_{\infty} \frac{\mathbf{J}(\mathbf{r}', t - |\mathbf{r} - \mathbf{r}'|)}{4\pi|\mathbf{r} - \mathbf{r}'|} d^3\mathbf{r}', \quad (1.87)$$

$$\mathbf{B} = \nabla \times \iiint_{\infty} \frac{\mathbf{J}(\mathbf{r}', t - |\mathbf{r} - \mathbf{r}'|)}{4\pi|\mathbf{r} - \mathbf{r}'|} d^3\mathbf{r}', \quad (1.88)$$

in any gauge.

1.3 Quantum electrodynamics

In §2, §3 and §5, we delve occasionally into the quantum domain. In the present section, we therefore outline some pertinent results from the theory of quantum electrodynamics [11–13].

We treat the particles non relativistically¹¹ and suppose that they reside together with the electromagnetic field in a cubic quantisation cavity of length L and hence, volume $V = L^3$. Imposing periodic boundary conditions upon this cavity, we identify wavevectors \mathbf{k} given by

$$\mathbf{k} = 2\pi(n_x\hat{\mathbf{x}} + n_y\hat{\mathbf{y}} + n_z\hat{\mathbf{z}})/L, \quad (1.89)$$

with $n_x, n_y, n_z \in \{0, \pm 1, \dots\}$. When appropriate, we then take the limit $L \rightarrow \infty$ of an infinitely large cubic quantisation cavity, in which

$$\sum_{\mathbf{k}} \rightarrow \iiint_{\infty} \frac{V}{8\pi^3} d^3\mathbf{k}. \quad (1.90)$$

We utilise the minimal coupling formalism in the Coulomb gauge and employ the Schrödinger picture of time dependence, unless otherwise stated. The Coulomb gauge is a natural choice for the low-energy description of molecules and atoms. In it, the scalar potential Φ is associated with the longitudinal piece \mathbf{E}^{\parallel} of the electric field \mathbf{E} . Φ thus embodies the non-retarded Coulomb interactions between the particles and can be eliminated from explicit consideration in favour of the particle trajectories \mathbf{r}_n [11]. In addition, the magnetic vector potential \mathbf{A} is equal to its solenoidal, gauge-invariant piece \mathbf{A}^{\perp} and is associated with the transverse piece \mathbf{E}^{\perp} of \mathbf{E} as well as with the magnetic flux density \mathbf{B} . \mathbf{A} thus embodies the radiation field, which in turn contains the entirety of the dynamical

¹¹A relativistic quantum-mechanical treatment of the particles would require us to delve into the realms of quantum field theory, introducing the Dirac field for electrons etc [11]. The non-relativistic treatment that we employ instead is sufficient, however, for the low energy description of molecules and atoms with which we content ourselves [11, 12].

freedom of the electromagnetic field, as described in §1.2.5.

1.3.1 Operators, state spaces and states

Regarding the particles, we introduce the operators $\hat{\mathbf{r}}_n = \mathbf{r}_n$ and $\hat{\mathbf{p}}_n = -i\hbar\nabla$ representing the position \mathbf{r}_n and canonical linear momentum $\mathbf{p}_n = m_n\dot{\mathbf{r}}_n + q_n\mathbf{A}(\mathbf{r}_n, t)$ of the n th particle¹².

Regarding the light, we introduce the components $\hat{a}_{\mathbf{k}(a)}$ and $\hat{a}_{\mathbf{k}(a)}^\dagger$ of the transverse ($\mathbf{k} \cdot \hat{\mathbf{a}}_{\mathbf{k}} = 0$) operators $\hat{\mathbf{a}}_{\mathbf{k}}$ and their Hermitian conjugates $\hat{\mathbf{a}}_{\mathbf{k}}^\dagger$ through the commutation relations [11, 12]

$$[\hat{a}_{\mathbf{k}(a)}, \hat{a}_{\mathbf{k}'(b)}] = 0, \quad (1.91)$$

$$[\hat{a}_{\mathbf{k}(a)}, \hat{a}_{\mathbf{k}'(b)}^\dagger] = \delta_{\mathbf{k}\mathbf{k}'} [\delta_{(ab)} - \hat{k}_{(a)}\hat{k}_{(b)}], \quad (1.92)$$

$$[\hat{a}_{\mathbf{k}(a)}^\dagger, \hat{a}_{\mathbf{k}'(b)}^\dagger] = 0, \quad (1.93)$$

with $\delta_{\mathbf{k}\mathbf{k}'}$ a Kronecker delta function. In the limit $L \rightarrow \infty$ of an infinitely large cubic quantisation cavity, the operators $\sqrt{\hbar V/2\pi^3}\hat{\mathbf{a}}_{\mathbf{k}}/2$ and $\sqrt{\hbar V/2\pi^3}\hat{\mathbf{a}}_{\mathbf{k}}^\dagger/2$ represent the normal variables $\tilde{\alpha}$ and their complex conjugates $\tilde{\alpha}^*$ [11].

The operators $\hat{\rho} = \hat{\rho}(\mathbf{r})$ and $\hat{\mathbf{J}} = \hat{\mathbf{J}}(\mathbf{r})$ representing the charge density ρ and the current density \mathbf{J} are

$$\hat{\rho} = \sum_{n=1}^N q_n \delta^3(\mathbf{r} - \hat{\mathbf{r}}_n), \quad (1.94)$$

$$\hat{\mathbf{J}} = \sum_{n=1}^N q_n \frac{1}{2} [\hat{\mathbf{r}}_n \delta^3(\mathbf{r} - \hat{\mathbf{r}}_n) + \delta^3(\mathbf{r} - \hat{\mathbf{r}}_n) \hat{\mathbf{r}}_n], \quad (1.95)$$

with $\hat{\mathbf{r}}_n$ the operator representing the velocity $\dot{\mathbf{r}}_n$ of the n th particle. Note the symmetrisation of $\hat{\mathbf{J}}$, which ensures that $\hat{\mathbf{J}}$ is Hermitian ($\hat{\mathbf{J}} = \hat{\mathbf{J}}^\dagger$). The operators $\hat{\mathbf{E}}^\perp = \hat{\mathbf{E}}^\perp(\mathbf{r})$, $\hat{\mathbf{B}} = \hat{\mathbf{B}}(\mathbf{r})$ and $\hat{\mathbf{A}} = \hat{\mathbf{A}}(\mathbf{r})$ representing the solenoidal piece \mathbf{E}^\perp of the electric field \mathbf{E} , the magnetic flux density \mathbf{B} and \mathbf{A} are

$$\hat{\mathbf{E}}^\perp = \sum_{\mathbf{k}} i \sqrt{\frac{\hbar|\mathbf{k}|}{2V}} [\hat{\mathbf{a}}_{\mathbf{k}} \exp(i\mathbf{k} \cdot \mathbf{r}) - \hat{\mathbf{a}}_{\mathbf{k}}^\dagger \exp(-i\mathbf{k} \cdot \mathbf{r})], \quad (1.96)$$

$$\hat{\mathbf{B}} = \sum_{\mathbf{k}} i \sqrt{\frac{\hbar}{2|\mathbf{k}|V}} \mathbf{k} \times [\hat{\mathbf{a}}_{\mathbf{k}} \exp(i\mathbf{k} \cdot \mathbf{r}) - \hat{\mathbf{a}}_{\mathbf{k}}^\dagger \exp(-i\mathbf{k} \cdot \mathbf{r})], \quad (1.97)$$

$$\hat{\mathbf{A}} = \sum_{\mathbf{k}} \sqrt{\frac{\hbar}{2|\mathbf{k}|V}} [\hat{\mathbf{a}}_{\mathbf{k}} \exp(i\mathbf{k} \cdot \mathbf{r}) + \hat{\mathbf{a}}_{\mathbf{k}}^\dagger \exp(-i\mathbf{k} \cdot \mathbf{r})], \quad (1.98)$$

¹²These forms are correct in the position representation [11, 14, 27].

whilst the operator $\hat{\mathbf{E}}^{\parallel} = \hat{\mathbf{E}}^{\parallel}(\mathbf{r})$ representing the irrotational piece \mathbf{E}^{\parallel} of \mathbf{E} is

$$\begin{aligned}\hat{\mathbf{E}}^{\parallel} &= \iiint_V \frac{\hat{\rho}(\mathbf{r}')(\mathbf{r} - \mathbf{r}')}{4\pi|\mathbf{r} - \mathbf{r}'|^3} d^3\mathbf{r}' \\ &= \sum_{n=1}^N \frac{q_n(\mathbf{r} - \hat{\mathbf{r}}_n)}{4\pi|\mathbf{r} - \hat{\mathbf{r}}_n|^3}.\end{aligned}\quad (1.99)$$

Of particular importance, as it governs time evolution, is the operator \hat{H} representing the Hamiltonian, which is [11, 12]

$$\begin{aligned}\hat{H} &= \sum_{n=1}^N \frac{[\hat{\mathbf{p}}_n - q_n \hat{\mathbf{A}}(\hat{\mathbf{r}}_n)]^2}{2m_n} \\ &\quad + \sum_{n=1}^N \sum_{n'=1}^N \frac{q_n q_{n'}}{8\pi|\hat{\mathbf{r}}_n - \hat{\mathbf{r}}_{n'}|} \\ &\quad + \iiint_V \frac{1}{2} (\hat{\Pi}^2 + |\hat{\nabla} \times \hat{\mathbf{A}}|^2) d^3\mathbf{r},\end{aligned}\quad (1.100)$$

with $\hat{\Pi} = -\hat{\mathbf{E}}^{\perp}$ the operator representing the momentum density conjugate to $\hat{\mathbf{A}}$. The first term seen on the right-hand side of (1.100) describes the kinetic energies of the particles, the second term describes the electrostatic Coulomb self energies of the particles (which are diverging constants) as well as the electrostatic Coulomb energies shared between the particles and the third term describes the energy of the radiation field.

For our purposes, it suffices to consider an expansion of the radiation field in terms of circularly polarised plane-wave ‘modes’. Thus, we associate with each wavevector \mathbf{k} , left- and right-handed circular polarisations, labeled with a polarisation parameter $\sigma = \pm 1$ and defined by complex polarisation vectors $\tilde{\mathbf{e}}_{\mathbf{k}\sigma}$ which are transverse ($\mathbf{k} \cdot \tilde{\mathbf{e}}_{\mathbf{k}\sigma} = 0$) and orthonormal ($\tilde{\mathbf{e}}_{\mathbf{k}\sigma} \cdot \tilde{\mathbf{e}}_{\mathbf{k}\sigma'}^* = \delta_{\sigma\sigma'}$) [11, 12]. Taking

$$\hat{\mathbf{a}}_{\mathbf{k}} = \sum_{\sigma} \tilde{\mathbf{e}}_{\mathbf{k}\sigma} \hat{a}_{\mathbf{k}\sigma}, \quad (1.101)$$

the Bosonic commutation relations

$$[\hat{a}_{\mathbf{k}\sigma}, \hat{a}_{\mathbf{k}'\sigma'}] = 0, \quad (1.102)$$

$$[\hat{a}_{\mathbf{k}\sigma}, \hat{a}_{\mathbf{k}'\sigma'}^{\dagger}] = \delta_{\mathbf{k}\mathbf{k}'} \delta_{\sigma\sigma'}, \quad (1.103)$$

$$[\hat{a}_{\mathbf{k}\sigma}^{\dagger}, \hat{a}_{\mathbf{k}'\sigma'}^{\dagger}] = 0, \quad (1.104)$$

then follow from the commutation relations (1.91)-(1.93) and we identify $\hat{a}_{\mathbf{k}\sigma}$ and $\hat{a}_{\mathbf{k}\sigma}^{\dagger}$ as annihilation and creation operators for a circularly polarised plane-wave-mode photon of wavevector \mathbf{k} and polarisation parameter σ [11–13]. Other mode expansions with their associated photons may also be considered a priori or obtained from the above via appropriate unitary transformations [11, 28].

The state space Ξ of the system is the product of the state spaces Ξ_n in which the $\hat{\mathbf{r}}_n$ and $\hat{\mathbf{p}}_n$ act and the state spaces $\Xi_{\mathbf{k}\sigma}$ in which the $\hat{a}_{\mathbf{k}\sigma}$ and $\hat{a}_{\mathbf{k}\sigma}^\dagger$ act. Of particular use to us are the photon number states $|n_{\mathbf{k}\sigma}\rangle$ ($n_{\mathbf{k}\sigma} = 0, 1, \dots$) which we take to satisfy

$$\hat{a}_{\mathbf{k}\sigma}|n_{\mathbf{k}\sigma}\rangle = \sqrt{n_{\mathbf{k}\sigma}}|n_{\mathbf{k}\sigma} - 1\rangle, \quad (1.105)$$

$$\hat{a}_{\mathbf{k}\sigma}^\dagger|n_{\mathbf{k}\sigma}\rangle = \sqrt{n_{\mathbf{k}\sigma} + 1}|n_{\mathbf{k}\sigma} + 1\rangle, \quad (1.106)$$

and which constitute a complete ($\sum_{n_{\mathbf{k}\sigma}=0}^{\infty} |n_{\mathbf{k}\sigma}\rangle\langle n_{\mathbf{k}\sigma}| = 1$) and orthonormal ($\langle n_{\mathbf{k}\sigma}|n'_{\mathbf{k}\sigma}\rangle = \delta_{n_{\mathbf{k}\sigma}n'_{\mathbf{k}\sigma}}$) basis for $\Xi_{\mathbf{k}\sigma}$ [11–13].

1.3.2 The classical limit

The correspondance between the quantum and classical theories of electrodynamics is perhaps clearer in the Heisenberg picture of time dependence rather than the Schrödinger picture of time dependence, in which it is found that [11, 13]

$$m_n \hat{\mathbf{r}}_n = q_n \left\{ \hat{\mathbf{E}}(\hat{\mathbf{r}}_n) + \frac{1}{2} \left[\hat{\mathbf{r}}_n \times \hat{\mathbf{B}}(\hat{\mathbf{r}}_n) - \hat{\mathbf{B}}(\hat{\mathbf{r}}_n) \times \hat{\mathbf{r}}_n \right] \right\} \quad (1.107)$$

with $\hat{\mathbf{r}}_n$ the operator representing the acceleration $\ddot{\mathbf{r}}_n$ of the n th particle and

$$\nabla \cdot \hat{\mathbf{E}} = \hat{\rho}, \quad (1.108)$$

$$\nabla \cdot \hat{\mathbf{B}} = 0, \quad (1.109)$$

$$\nabla \times \hat{\mathbf{E}} = -\hat{\dot{\mathbf{B}}}, \quad (1.110)$$

$$\nabla \times \hat{\mathbf{B}} = \hat{\mathbf{J}} + \hat{\dot{\mathbf{E}}}, \quad (1.111)$$

with $\hat{\dot{\mathbf{B}}}$ and $\hat{\dot{\mathbf{E}}}$ the operators representing the time derivatives $\dot{\mathbf{B}}$ and $\dot{\mathbf{E}}$ of \mathbf{B} and \mathbf{E} . Clearly, (1.107) resembles the Newton-Einstein-Lorentz equation (1.3) and (1.108)-(1.111) resemble Maxwell's equations (1.4)-(1.7).

In accord with the correspondance principle, there exist limits in which the theory of quantum electrodynamics *reduces*, in essence, to the theory of classical electrodynamics, as we now elucidate. Our goal here is to construct a state $|\Psi(0)\rangle$ of the system at time $t = 0$ say, such that the expectation values of appropriate quantum mechanical operators closely resemble the classical quantities presented in §1.2. To this end, let us first consider a single mode of the radiation field, of wavevector \mathbf{k} and polarisation parameter σ . The coherent state

$$|\tilde{\alpha}_{\mathbf{k}\sigma}\rangle = \exp(-|\tilde{\alpha}_{\mathbf{k}\sigma}|^2/2) \sum_{n_{\mathbf{k}\sigma}=0}^{\infty} \frac{\tilde{\alpha}_{\mathbf{k}\sigma}^{n_{\mathbf{k}\sigma}}}{\sqrt{n_{\mathbf{k}\sigma}!}} |n_{\mathbf{k}\sigma}\rangle, \quad (1.112)$$

due to Schrödinger [11, 12, 29], is an eigenstate of the annihilation operator $\hat{a}_{\mathbf{k}\sigma}$ with eigenvalue $\tilde{\alpha}_{\mathbf{k}\sigma}$:

$$\hat{a}_{\mathbf{k}\sigma}|\tilde{\alpha}_{\mathbf{k}\sigma}\rangle = \tilde{\alpha}_{\mathbf{k}\sigma}|\tilde{\alpha}_{\mathbf{k}\sigma}\rangle. \quad (1.113)$$

Supposing that all modes of the radiation field occupy coherent states, we have in effect that

$$\begin{aligned}\hat{a}_{\mathbf{k}\sigma} &\rightarrow \tilde{\alpha}_{\mathbf{k}\sigma} \\ \hat{a}_{\mathbf{k}\sigma}^\dagger &\rightarrow \tilde{\alpha}_{\mathbf{k}\sigma}^*.\end{aligned}\tag{1.114}$$

In the limit $L \rightarrow \infty$ of an infinitely large cubic quantisation volume, we can then identify the quantities $\sqrt{\hbar V/2\pi^3} \sum_{\sigma} \tilde{\mathbf{e}}_{\mathbf{k}\sigma} \tilde{\alpha}_{\mathbf{k}\sigma}/2$ and $\sqrt{\hbar V/2\pi^3} \sum_{\sigma} \tilde{\mathbf{e}}_{\mathbf{k}\sigma}^* \tilde{\alpha}_{\mathbf{k}\sigma}^*/2$ with the classical normal variables $\tilde{\alpha}(\mathbf{k}, 0)$ and their complex conjugates $\tilde{\alpha}^*(\mathbf{k}, 0)$ at $t = 0$. If, in addition, the particles occupy localised wave packet states, the motions of which resemble classical trajectories¹³ [30], a picture resembling that presented in §1.2 is recovered, as desired.

1.3.3 Solutions

The evolution of the state $|\Psi\rangle = |\Psi(t)\rangle$ of the system is governed by Schrödinger's equation [11–13, 30]:

$$i\hbar|\dot{\Psi}\rangle = \hat{H}|\Psi\rangle.\tag{1.115}$$

In principle, this may be solved by identifying the eigenstates $|s\rangle$ and associated eigenvalues $\hbar\omega_s$ of \hat{H} , which satisfy

$$\hat{H}|s\rangle = \hbar\omega_s|s\rangle\tag{1.116}$$

and are taken by us to be complete ($\sum_s |s\rangle\langle s| = 1$) and orthonormal ($\langle s|s'\rangle = \delta_{ss'}$). We then have that

$$|\Psi\rangle = \sum_s \tilde{a}_s \exp(-i\omega_s t) |s\rangle\tag{1.117}$$

which is normalised ($\langle\Psi|\Psi\rangle = 1$) provided the probability amplitudes \tilde{a}_s satisfy $\sum_s |\tilde{a}_s|^2 = 1$.

In practice, this approach is intractable in general and we must resort instead to approximate methods of solution which we now outline whilst considering a single molecule or atom. We begin by partitioning \hat{H} as [11, 12]

$$\hat{H} = \hat{H}_0 + \hat{V}\tag{1.118}$$

with the operator \hat{H}_0 describing the molecule or atom and the radiation field *decoupled* from each other, as

$$\hat{H}_0 = \hat{H}_{\text{mol}} + \hat{H}_{\text{rad}}\tag{1.119}$$

¹³More formally, the $\hat{\mathbf{r}}_n$ may be replaced with their expectation values $\langle\hat{\mathbf{r}}_n\rangle$ provided variances and analogous quantities are sufficiently small such that $\langle f(\hat{\mathbf{r}}_n) \rangle = \langle f(\langle\hat{\mathbf{r}}_n\rangle) + (\hat{\mathbf{r}}_n - \langle\hat{\mathbf{r}}_n\rangle)_{(a)} \partial f(\langle\hat{\mathbf{r}}_n\rangle) / \partial \langle\hat{\mathbf{r}}_n\rangle_{(a)} + \frac{1}{2}(\hat{\mathbf{r}}_n - \langle\hat{\mathbf{r}}_n\rangle)_{(a)}(\hat{\mathbf{r}}_n - \langle\hat{\mathbf{r}}_n\rangle)_{(b)} \partial^2 f(\langle\hat{\mathbf{r}}_n\rangle) / \partial \langle\hat{\mathbf{r}}_n\rangle_{(a)} \partial \langle\hat{\mathbf{r}}_n\rangle_{(b)} + \dots \rangle = f(\langle\hat{\mathbf{r}}_n\rangle) + \frac{1}{2} \langle (\hat{\mathbf{r}}_n - \langle\hat{\mathbf{r}}_n\rangle)_{(a)}(\hat{\mathbf{r}}_n - \langle\hat{\mathbf{r}}_n\rangle)_{(b)} \rangle \partial^2 f(\langle\hat{\mathbf{r}}_n\rangle) / \partial \langle\hat{\mathbf{r}}_n\rangle_{(a)} \partial \langle\hat{\mathbf{r}}_n\rangle_{(b)} + \dots \approx f(\langle\hat{\mathbf{r}}_n\rangle)$ for the functions f of interest.

with

$$\hat{H}_{\text{mol}} = \sum_{n=1}^N \frac{\hat{\mathbf{p}}_n^2}{2m_n} + \sum_{n=1}^N \sum_{n'=1}^N \frac{q_n q_{n'}}{8\pi |\hat{\mathbf{r}}_n - \hat{\mathbf{r}}_{n'}|}, \quad (1.120)$$

$$\hat{H}_{\text{rad}} = \iiint_V \frac{1}{2} \left(\hat{\mathbf{\Pi}}^2 + |\nabla \times \hat{\mathbf{A}}|^2 \right) d^3\mathbf{r}, \quad (1.121)$$

whilst the operator \hat{V} describes the *interaction* between the molecule or atom and the radiation field, as

$$\hat{V} = - \sum_{n=1}^N \frac{q_n}{m_n} \hat{\mathbf{p}}_n \cdot \hat{\mathbf{A}}(\hat{\mathbf{r}}_n) + \sum_{n=1}^N \frac{q_n^2}{2m_n} \left| \hat{\mathbf{A}}(\hat{\mathbf{r}}_n) \right|^2. \quad (1.122)$$

The problem posed by \hat{H}_0 alone may be *solved* as follows. Let us assume that the eigentates $|k\rangle$ and associated eigenvalues $\hbar\omega_k$ ($k = 0, 1, \dots$) of \hat{H}_{mol} are known:

$$\hat{H}_{\text{mol}}|k\rangle = \hbar\omega_k|k\rangle, \quad (1.123)$$

and that they are complete ($\sum_{k=0}^{\infty} |k\rangle\langle k| = 1$) and orthonormal ($\langle k|k'\rangle = \delta_{kk'}$). We let $k = 0$ in particular denote the molecular or atomic ground state. The eigenspectrum of \hat{H}_{rad} is comprised of photon number states $|\{n_{\mathbf{k}\sigma}\}\rangle$ as

$$\hat{H}_{\text{rad}}|\{n_{\mathbf{k}\sigma}\}\rangle = \left[\sum_{\mathbf{k}} \sum_{\sigma} \hbar|\mathbf{k}|n_{\mathbf{k}\sigma} + \mathcal{Z}^{(0)} \right] |\{n_{\mathbf{k}\sigma}\}\rangle, \quad (1.124)$$

with $\mathcal{Z}^{(0)} = \sum_{\mathbf{k}} \hbar c|\mathbf{k}|$ the electromagnetic energy of the vacuum, which is a diverging constant. The eigenstates $|s^{(0)}\rangle$ and associated eigenvalues $\hbar\omega_s^{(0)}$ of \hat{H}_0 follow simply as

$$\hat{H}_0|s^{(0)}\rangle = \hbar\omega_s^{(0)}|s^{(0)}\rangle, \quad (1.125)$$

with

$$\left\{ |s^{(0)}\rangle \right\} = \left\{ |k\rangle |\{n_{\mathbf{k}\sigma}\}\rangle \right\}, \quad (1.126)$$

$$\left\{ \hbar\omega_s^{(0)} \right\} = \left\{ \hbar\omega_k + \sum_{\mathbf{k}} \sum_{\sigma} \hbar c|\mathbf{k}|n_{\mathbf{k}\sigma} + \mathcal{Z}^{(0)} \right\}. \quad (1.127)$$

We can now employ the $|s^{(0)}\rangle$ and $\hbar\omega_s^{(0)}$ as a basis in which to tackle the full problem posed by \hat{H} . In doing so, use can be made under many circumstances of two approximations.

The first approximation follows from the assumption that the photon numbers $n_{\mathbf{k}\sigma}$ under consideration are such that the strength of the radiation field can be regarded as being less than that of the Coulomb field binding the molecule or atom together [11, 12]: this justifies seeking solutions in powers of \hat{V} or perhaps instead in powers of the charge e of a proton, say. Time-independent perturbation theory may be employed to calculate energy shifts and other such ‘static’ quantities and

reveals for example that [27, 30]

$$|s\rangle = |s^{(0)}\rangle + \sum_{s' \neq s} \frac{\langle s'^{(0)} | \hat{V} | s^{(0)} \rangle}{\hbar \omega_{ss'}^{(0)}} |s'^{(0)}\rangle, \quad (1.128)$$

$$\hbar \omega_s = \hbar \omega_s^{(0)} + \langle s^{(0)} | \hat{V} | s^{(0)} \rangle + \sum_{s' \neq s} \frac{\langle s^{(0)} | \hat{V} | s'^{(0)} \rangle \langle s'^{(0)} | \hat{V} | s^{(0)} \rangle}{\hbar \omega_{ss'}^{(0)}}, \quad (1.129)$$

to first order in \hat{V} for $|s\rangle$ and second order in \hat{V} for $\hbar \omega_s$. Here we have introduced the notation $\omega_{ss'}^{(0)} = \omega_s^{(0)} - \omega_{s'}^{(0)}$. Dirac's method of the variation of constants may be employed to calculate transition rates and other such 'dynamic' quantities and reveals for example that [13, 27, 31]

$$|\Psi\rangle = \sum_s \tilde{b}_s \exp[-i\omega_s^{(0)}t] |s^{(0)}\rangle, \quad (1.130)$$

with the probability amplitudes $\tilde{b}_s = \tilde{b}_s(t)$ given in terms of their values at $t = 0$ as

$$\tilde{b}_s(t) = \tilde{b}_s(0) - \sum_{s' \neq s} \frac{\tilde{b}_{s'}(0)}{\hbar \omega_{ss'}^{(0)}} \left\{ \exp[i\omega_{ss'}^{(0)}t] - 1 \right\} \langle s^{(0)} | \hat{V} | s'^{(0)} \rangle \quad (1.131)$$

to first order in \hat{V} .

The second approximation follows from the assumption that the molecule or atom is smaller than the length scales $2\pi/|\mathbf{k}|$ associated with relevant modes of the radiation field: this justifies an expansion of the ' $\mathbf{p} \cdot \mathbf{A}$ ' contributions to \hat{V} in terms of the multipole moments of the charge and current distributions of the molecule or atom as¹⁴ [12, 13, 25]

$$\begin{aligned} \hat{V} = & \sum_{i=1}^{\infty} \frac{i}{\hbar} \left[\hat{d}_{(a_1 a_2 \dots a_i)}^{(i)}, \hat{H}_{\text{mol}} \right] \partial_{a_2} \dots \partial_{a_i} \hat{A}_{(a_1)}(\mathbf{R}) \\ & - \sum_{i=1}^{\infty} \hat{m}_{(a_1 a_2 \dots a_i)}^{(i)} \partial_{a_2} \dots \partial_{a_i} \hat{B}_{(a_1)}(\mathbf{R}) \\ & + \sum_{n=1}^N \frac{q_n^2}{2m_n} \left| \hat{\mathbf{A}}(\hat{\mathbf{r}}_n) \right|^2, \end{aligned} \quad (1.132)$$

with the operators $\hat{d}_{(a_1 a_2 \dots a_i)}^{(i)}$ representing the components $d_{(a_1 a_2 \dots a_i)}^{(i)}$ of the i th electric multipole moment of the molecule or atom's charge distribution and the operators $\hat{m}_{(a_1 a_2 \dots a_i)}^{(i)}$ representing the components of the i th canonical magnetic multipole moment of the molecule or atom's current

¹⁴Although they do not make natural appearances in the non-relativistic regime, the spins of the electrons and also the nuclei can be accounted for in a heuristic manner by adding appropriate contributions to the operators $\hat{m}_{(a)}^{(1)}$ representing the components of the canonical magnetic dipole moment of the molecule or atom.

distribution given by

$$\hat{d}_{(a_1 a_2 \dots a_i)}^{(i)} = \sum_{n=1}^N \frac{q_n}{i!} (\hat{\mathbf{r}}_n - \mathbf{R})_{(a_1)} (\hat{\mathbf{r}}_n - \mathbf{R})_{(a_2)} \dots (\hat{\mathbf{r}}_n - \mathbf{R})_{(a_i)}, \quad (1.133)$$

$$\hat{m}_{(a_1 a_2 \dots a_i)}^{(i)} = \sum_{n=1}^N \frac{q_n i}{m_n (i+1)!} [(\hat{\mathbf{r}}_n - \mathbf{R}) \times \hat{\mathbf{p}}_n]_{(a_1)} (\hat{\mathbf{r}}_n - \mathbf{R})_{(a_2)} \dots (\hat{\mathbf{r}}_n - \mathbf{R})_{(a_i)}, \quad (1.134)$$

where we have taken the centre of mass of the molecule or atom and the origin \mathbf{R} of our multipole expansion to be fixed and have supposed that the latter coincides with the position of the former or resides somewhere near it. Retention of the contribution made to \hat{V} by $\hat{d}_{(a)}^{(1)}$ only constitutes the electric dipole approximation, due to Silberstein [32]. It will be noticed that we have refrained from expanding the $|\mathbf{A}|^2$ or diamagnetic contribution to \hat{V} .

1.4 The semiclassical approximation and induced multipole moments

The semiclassical approximation, in which the inner workings of molecule(s) and / or atom(s) are treated quantum mechanically as in §1.3 whilst the electromagnetic field is otherwise treated classically as in §1.2 and is regarded as being an externally imposed influence acting upon the molecule(s) and / or atom(s) [12], makes tractable a scenario that will be of particular interest to us in §5.

Specifically, let us consider a single molecule or atom, treated non-relativistically, the centre of mass of which we take to be fixed at or near some position \mathbf{R} in the presence of weak, monochromatic, off-resonance light of angular frequency $\omega = c|\mathbf{k}|$ that is (otherwise) freely propagating and the length scale $2\pi/|\mathbf{k}|$ associated with which is larger than the molecule or atom. Thus, the electric field \mathbf{E} and magnetic flux density \mathbf{B} comprising the light are described by (1.75)-(1.80). We suppose that the molecule or atom occupies its ground state $|0\rangle$ at time $t = -\infty$ and that it is subsequently introduced to the light in an adiabatic manner. Under these circumstances, the light simply induces oscillations in the charge and current distributions of the molecule or atom [25, 33]. The semiclassical approximation enables us to obtain explicit expressions that describe these oscillations within the classical domain but which nevertheless reflect the quantum mechanical structure of the molecule or atom: we work to order e^2 and identify the components $d_{(a_1 a_2 \dots a_i)}^{(i)}$ of the i th electric multipole moment of the molecule or atom's charge distribution and the components $m_{(a_1 a_2 \dots a_i)}^{(i)}$ of the i th magnetic multipole moment of the molecule or atoms's current distribution, taken about \mathbf{R} , with quantum mechanical expectation values as

$$d_{(a_1 a_2 \dots a_i)}^{(i)} = \langle \Psi | \hat{d}_{(a_1 a_2 \dots a_i)}^{(i)} | \Psi \rangle, \quad (1.135)$$

$$m_{(a_1 a_2 \dots a_i)}^{(i)} = \langle \Psi | \hat{m}_{(a_1 a_2 \dots a_i)}^{(i)} | \Psi \rangle - \langle 0 | \sum_{n=1}^N \frac{q_n^2 i}{m_n (i+1)!} [(\hat{\mathbf{r}}_n - \mathbf{R}) \times \mathbf{A}(\hat{\mathbf{r}}_n, t)]_{a_1} (\hat{\mathbf{r}}_n - \mathbf{R})_{a_2} \dots (\hat{\mathbf{r}}_n - \mathbf{R})_{a_i} | 0 \rangle, \quad (1.136)$$

with the state $|\Psi\rangle$ of the molecule or atom obtained to the required level of approximation using Dirac's method of the variation of constants [13, 27, 31], say.

For ω in the visible or near infrared and a small molecule such as hexahelicene¹⁵ [25, 34, 35] or an atom, the leading order contributions to the calculations with which we will concern ourselves in §5 are obtained by truncating the components $P_{(a)}$ and $M_{(a)}$ of the multipole expansions of the polarisation \mathbf{P} and magnetisation \mathbf{M} attributable to the molecule or atom as [11, 12, 25]

$$P_{(a)} \approx \mu_{(a)} \delta^3(\mathbf{r} - \mathbf{R}) - \frac{1}{3} \Theta_{(ab)} \partial_b \delta^3(\mathbf{r} - \mathbf{R}) + \sum_{n=1}^N \frac{q_n}{2} \delta_{(ab)} |\mathbf{r}_n - \mathbf{R}|^2 \partial_b \delta^3(\mathbf{r} - \mathbf{R}), \quad (1.137)$$

$$M_{(a)} \approx m'_{(a)} \delta^3(\mathbf{r} - \mathbf{R}), \quad (1.138)$$

where, in a standard notation [25, 33], the components $\mu_{(a)} = d_{(a)}^{(1)}$ of the electric-dipole moment of the molecule or atom's charge distribution, the components $\Theta_{(ab)} = 3d_{(ab)}^{(2)} + \sum_{n=1}^N \delta_{(ab)} q_n |\mathbf{r}_n - \mathbf{R}|^2 / 2$ of the symmetric and traceless electric quadrupole moment of the molecule or atom's charge distribution and the components $m'_{(a)} = m_{(a)}'^{(1)}$ of the magnetic dipole moment of the molecule or atom's current distribution are given by

$$\mu_{(a)} \approx \langle 0 | \hat{\mu}_{(a)} | 0 \rangle + \Re [\tilde{\mu}_{(a)} \exp(-i\omega t)], \quad (1.139)$$

$$\Theta_{(ab)} \approx \langle 0 | \hat{\Theta}_{(ab)} | 0 \rangle + \Re [\tilde{\Theta}_{(ab)} \exp(-i\omega t)], \quad (1.140)$$

$$m'_{(a)} \approx \langle 0 | \hat{m}_{(a)} | 0 \rangle + \Re [\tilde{m}'_{(a)} \exp(-i\omega t)], \quad (1.141)$$

with the complex quantities $\tilde{\mu}_{(a)}$, $\tilde{\Theta}_{(ab)}$ and $\tilde{m}'_{(a)}$ related to the light in turn as

$$\tilde{\mu}_{(a)} = \tilde{\alpha}_{(ab)} \tilde{E}_{(b)}(\mathbf{R}) + \frac{1}{3} \tilde{A}_{(abc)} \partial_b \tilde{E}_{(c)}(\mathbf{R}) + \tilde{G}_{(ab)} \tilde{B}_{(b)}(\mathbf{R}), \quad (1.142)$$

$$\tilde{\Theta}_{(ab)} = \tilde{\mathcal{A}}_{(cab)} \tilde{E}_{(c)}(\mathbf{R}), \quad (1.143)$$

$$\tilde{m}'_{(a)} = \tilde{\mathcal{G}}_{(ba)} \tilde{E}_{(b)}(\mathbf{R}). \quad (1.144)$$

The complex polarisabilities $\tilde{\alpha}_{(ab)} = \tilde{\alpha}_{(ab)}(\omega)$, $\tilde{A}_{(abc)} = \tilde{A}_{(abc)}(\omega)$, $\tilde{\mathcal{A}}_{(abc)} = \tilde{\mathcal{A}}_{(abc)}(\omega)$, $\tilde{G}_{(ab)} = \tilde{G}_{(ab)}(\omega)$ and $\tilde{\mathcal{G}}_{(ab)} = \tilde{\mathcal{G}}_{(ab)}(\omega)$ are

$$\tilde{\alpha}_{(ab)} = \alpha_{(ab)} - i\alpha'_{(ab)}, \quad (1.145)$$

$$\tilde{A}_{(abc)} = A_{(abc)} - iA'_{(abc)}, \quad (1.146)$$

$$\tilde{\mathcal{A}}_{(abc)} = \mathcal{A}_{(abc)} + i\mathcal{A}'_{(abc)}, \quad (1.147)$$

$$\tilde{G}_{(ab)} = G_{(ab)} - iG'_{(ab)}, \quad (1.148)$$

$$\tilde{\mathcal{G}}_{(ab)} = \mathcal{G}_{(ab)} + i\mathcal{G}'_{(ab)}, \quad (1.149)$$

with the real polarisabilities $\alpha_{(ab)} = \alpha_{(ab)}(\omega)$, $\alpha'_{(ab)} = \alpha'_{(ab)}(\omega)$, $A_{(abc)} = A_{(abc)}(\omega)$, $A'_{(abc)} = A'_{(abc)}(\omega)$, $G_{(ab)} = G_{(ab)}(\omega)$ and $\mathcal{G}_{(ab)} = \mathcal{G}_{(ab)}(\omega)$ related to the quantum-mechanical inner workings

¹⁵We consider hexahelicene in particular in §5.

of the molecule or atom as [25, 33]

$$\alpha_{(ab)} = \sum_{k \neq 0}^{\infty} \frac{2}{\hbar} \omega_{k0} f_{k0} \Re \left[\langle 0 | \hat{\mu}_{(a)} | k \rangle \langle k | \hat{\mu}_{(b)} | 0 \rangle \right], \quad (1.150)$$

$$\alpha'_{(ab)} = - \sum_{k \neq 0}^{\infty} \frac{2}{\hbar} \omega_{k0} f_{k0} \Im \left[\langle 0 | \hat{\mu}_{(a)} | k \rangle \langle k | \hat{\mu}_{(b)} | 0 \rangle \right], \quad (1.151)$$

$$A_{(abc)} = \sum_{k \neq 0}^{\infty} \frac{2}{\hbar} \omega_{k0} f_{k0} \Re \left[\langle 0 | \hat{\mu}_{(a)} | k \rangle \langle k | \hat{\Theta}_{(bc)} | 0 \rangle \right], \quad (1.152)$$

$$A'_{(abc)} = - \sum_{k \neq 0}^{\infty} \frac{2}{\hbar} \omega_{k0} f_{k0} \Im \left[\langle 0 | \hat{\mu}_{(a)} | k \rangle \langle k | \hat{\Theta}_{(bc)} | 0 \rangle \right], \quad (1.153)$$

$$G_{(ab)} = \sum_{k \neq 0}^{\infty} \frac{2}{\hbar} \omega_{k0} f_{k0} \Re \left[\langle 0 | \hat{\mu}_{(a)} | k \rangle \langle k | \hat{m}_{(b)} | 0 \rangle \right], \quad (1.154)$$

$$G'_{(ab)} = - \sum_{k \neq 0}^{\infty} \frac{2}{\hbar} \omega_{k0} f_{k0} \Im \left[\langle 0 | \hat{\mu}_{(a)} | k \rangle \langle k | \hat{m}_{(b)} | 0 \rangle \right], \quad (1.155)$$

with \Im a function that yields the imaginary part of its argument and the so-called dispersion lineshape $f_{k0} = f_{k0}(\omega)$ associated with the $k \leftarrow 0$ molecular or atomic transition given here by

$$f_{k0} = \frac{1}{\omega_{k0}^2 - \omega^2}. \quad (1.156)$$

It is also convenient for us to introduce a complex quantity $\tilde{\zeta}_{abc} = \tilde{\zeta}_{abc}(\omega)$, as [25]

$$\begin{aligned} \tilde{\zeta}_{(abc)} = & \frac{1}{c} \left(\frac{\omega}{3} \left\{ A'_{(abc)} + A'_{(bac)} + i [A_{(abc)} - A_{(bac)}] \right\} \right. \\ & \left. + \epsilon_{(dca)} [G_{(bd)} + iG'_{(bd)}] + \epsilon_{(dcb)} [G_{(ad)} - iG'_{(ad)}] \right). \end{aligned} \quad (1.157)$$

The effects of externally imposed perturbations, such as a static electric field, as well as internal perturbations, such as spin-orbit coupling, can be incorporated into the present formalism in the manner exemplified in Barron's book [25], for example. Provided they are non-degenerate, as we have assumed them to be, the unperturbed wavefunctions of the molecule or atom can be taken to be real [25, 27] and the simplification $\alpha'_{(ab)} = A_{(abc)} = G_{(ab)} = 0$ then results. We will make tacit use of this. It is appropriate in some practical calculations to average molecular properties over all possible molecular orientations. We denote such isotropic averaging using angular brackets. Pertinent results in this regard can be found in Barron's book [25], as well as the book by Craig and Thirunamachandran [12], for example.

The semiclassical approximation suffers from certain deficiencies. In particular, the phenomenon of spontaneous emission is absent [12] and the expressions presented above lose validity and ultimately fail as ω approaches molecular or atomic transition angular frequencies $\omega_{kk'}$. Radiative

damping can be incorporated to some extent by taking

$$f_{k0} \rightarrow f_{k0} + ig_{k0} \quad (1.158)$$

with f_{k0} and the so-called absorption lineshape $g_{k0} = g_{k0}(\omega)$ associated with the $k \leftarrow 0$ molecular or atomic transition now given by

$$f_{k0} = \frac{\omega_{k0}^2 - \omega^2}{(\omega_{k0}^2 - \omega^2)^2 + \omega^2 \Gamma_{k0}^2}, \quad (1.159)$$

$$g_{k0} = \frac{\omega \Gamma_{k0}}{(\omega_{k0}^2 - \omega^2)^2 + \omega^2 \Gamma_{k0}^2}, \quad (1.160)$$

with Γ_{k0} an associated decay rate [25]. These forms (1.159) and (1.160) for f_{k0} and g_{k0} lead to the satisfaction of crossing relations etc as is demonstrated in Barron's book [25]. A more accurate description of damping processes is offered, however, by a master equation approach, wherein the molecule or atom is described by a density matrix and the effects of relaxation processes not readily incorporable in a Hamiltonian description, including spontaneous emission, may be accounted for with rigour [31].

1.5 Angular momentum: some terminology

In the currently established literature, an angular momentum is sometimes *defined* as being any time-odd pseudovector \mathbf{j} , the operators $\hat{j}_{(a)}$ representing the components $j_{(a)}$ of which satisfy the commutation relations [27]

$$[\hat{j}_{(a)}, \hat{j}_{(b)}] = i\hbar \epsilon_{(abc)} \hat{j}_{(c)}. \quad (1.161)$$

The familiar quantum-mechanical and hence classical description of angular momentum follows from these (1.161), including the identification of states $|j, m_j\rangle$ satisfying

$$(\hat{j}_x^2 + \hat{j}_y^2 + \hat{j}_z^2)|j, m_j\rangle = \hbar^2 j(j+1)|j, m_j\rangle, \quad (1.162)$$

$$\hat{j}_z|j, m_j\rangle = \hbar m_j|j, m_j\rangle, \quad (1.163)$$

for example, with $j \in \{0, 1/2, 1, \dots\}$ and $m_j \in \{-j, -j+1, \dots, j-1, j\}$ quantum numbers [27, 30].

Whilst this description certainly fits many angular momenta, I ask the reader to regard it with some apathy, for we will be led by the observations regarding light in §3 and §4 to suggest that the definition of an angular momentum seen in (1.161) is, in fact, overly restrictive. Rather, let us regard as being an angular momentum, *any* property of a system that is conserved by virtue of a rotational symmetry inherent in the equations of motion governing the system and thus possesses the dimensions of an angular momentum.

I use the terms *rotation* angular momentum and *boost* angular momentum to distinguish between

whether the rotation is of a *circular* nature (in space) or a *hyperbolic*¹⁶ nature (in spacetime). An angular momentum that is *not* dependent upon the location of the origin $x^\alpha = 0$ in spacetime is said to be *intrinsic* whereas an angular momentum that *is* dependent upon the location of $x^\alpha = 0$ is said instead to be *extrinsic*. The spin (rotation angular momentum) of a particle is thus intrinsic whereas the orbital (rotation) angular momentum of a particle is instead extrinsic. It should be noted, however, that ‘spin’ and ‘intrinsic’ are not synonymous in general, nor are ‘orbital’ and ‘extrinsic’. For example; the orbital angular momentum of a collection of more than one particle can be separated into a contribution attributable to the motion of the centre of energy, which is extrinsic, and a contribution relative to the centre of energy, which is intrinsic [14, 36].

¹⁶A boost can be regarded as a hyperbolic rotation in spacetime [10, 14], as is apparent in (1.18).

Chapter 2

Electric-Magnetic Democracy, the ‘Second Potential’ and the Structure of Maxwell’s Equations

2.1 Introduction

In the present chapter, we make some rather formal observations which underpin much of what follows in §3-§5. The text is based primarily upon my research papers [37] and [38].

2.2 In the strict absence of charge

Maxwell’s equations as written in the strict absence of charge:

$$\begin{aligned}\nabla \cdot \mathbf{E} &= 0, \\ \nabla \cdot \mathbf{B} &= 0, \\ \nabla \times \mathbf{E} &= -\dot{\mathbf{B}}, \\ \nabla \times \mathbf{B} &= \dot{\mathbf{E}},\end{aligned}$$

seen also in (1.68)-(1.71), favour neither the electric character nor the magnetic character of the freely propagating light that they describe. In particular, they retain their form under the transformation

$$\begin{aligned}\mathbf{E} &\rightarrow \mathbf{E} \cos \theta + \mathbf{B} \sin \theta \\ \mathbf{B} &\rightarrow \mathbf{B} \cos \theta - \mathbf{E} \sin \theta,\end{aligned}\tag{2.1}$$

for any time-odd Lorentz pseudoscalar angle θ , an observation due to Heaviside [39] and Larmor [40]. We refer to (2.1) accordingly as a Heaviside-Larmor rotation. One apparent reflection of this electric-magnetic democracy, a phrase coined by Berry [41], is the possibility of introducing, in addition to a scalar potential Φ and a magnetic vector potential \mathbf{A} , a pseudoscalar potential $\Theta = \Theta(\mathbf{r}, t)$ and an

electric pseudovector potential $\mathbf{C} = \mathbf{C}(\mathbf{r}, t)$ defined such that

$$\begin{aligned}\mathbf{E} &= -\nabla\Phi - \dot{\mathbf{A}} \\ &= -\nabla \times \mathbf{C},\end{aligned}\tag{2.2}$$

$$\begin{aligned}\mathbf{B} &= \nabla \times \mathbf{A} \\ &= -\nabla\Theta - \dot{\mathbf{C}},\end{aligned}\tag{2.3}$$

an observation due in essence to Bateman [42]. As far as the theory of special relativity is concerned, Θ and \mathbf{C} comprise an electric potential four-pseudovector $C^\alpha = (\Theta, \mathbf{C})$, in terms of which the electromagnetic field tensor $F^{\alpha\beta}$ and the dual electromagnetic field pseudotensor $G^{\alpha\beta}$ are

$$\begin{aligned}F^{\alpha\beta} &= \partial^\alpha A^\beta - \partial^\beta A^\alpha \\ &= -\epsilon^{\alpha\beta\gamma\delta} (\partial_\gamma C_\delta - \partial_\delta C_\gamma) / 2,\end{aligned}\tag{2.4}$$

$$\begin{aligned}G^{\alpha\beta} &= \epsilon^{\alpha\beta\gamma\delta} (\partial_\gamma A_\delta - \partial_\delta A_\gamma) / 2 \\ &= \partial^\alpha C^\beta - \partial^\beta C^\alpha.\end{aligned}\tag{2.5}$$

See also the book by Stratton [9] as well as the work of Anco and The [43] and the work of Barnett [44, 45]. Intriguingly, the *complete* set of Maxwell's equations as written in the strict absence of charge (1.68)-(1.71) follow from the definitions seen in (2.2) and (2.3) as well as in (2.4) and (2.5). Moreover, the electric field \mathbf{E} and the magnetic flux density \mathbf{B} are unchanged by the transformations

$$\begin{aligned}\Phi &\rightarrow \Phi + \dot{\chi} \\ \mathbf{A} &\rightarrow \mathbf{A} - \nabla\chi,\end{aligned}\tag{2.6}$$

$$\begin{aligned}\Theta &\rightarrow \Theta + \dot{\xi} \\ \mathbf{C} &\rightarrow \mathbf{C} - \nabla\xi,\end{aligned}\tag{2.7}$$

as was observed also by Anco and The [43]. It seems that there need not exist any particular relationship between the gauge function χ and the arbitrary time-even pseudoscalar field $\xi = \xi(\mathbf{r}, t)$. Taking

$$\begin{aligned}\Phi &\rightarrow \Phi \cos \theta + \Theta \sin \theta \\ \Theta &\rightarrow \Theta \cos \theta - \Phi \sin \theta \\ \mathbf{A} &\rightarrow \mathbf{A} \cos \theta + \mathbf{C} \sin \theta \\ \mathbf{C} &\rightarrow \mathbf{C} \cos \theta - \mathbf{A} \sin \theta,\end{aligned}\tag{2.8}$$

invokes a Heaviside-Larmor rotation (2.1).

As was highlighted in §1.2.5, a gauge transformation (1.13) (seen also in (2.6)) changes Φ and the irrotational piece \mathbf{A}^\parallel of \mathbf{A} whilst leaving the solenoidal piece \mathbf{A}^\perp of \mathbf{A} unchanged. Thus, Φ and \mathbf{A}^\parallel are not uniquely defined and it is these quantities *in particular* that suffer the gauge freedom of the electromagnetic field. Analogously, the transformation seen in (2.7) changes Θ and the irrota-

tional piece \mathbf{C}^{\parallel} of \mathbf{C} whilst leaving the solenoidal piece \mathbf{C}^{\perp} of \mathbf{C} unchanged. Thus, Θ and \mathbf{C}^{\parallel} are also not uniquely defined. This too may be appreciated in terms of gauge freedom by acknowledging electric-magnetic democracy: considering $\theta = \pi$ in (2.8), we argue that some *other* party could regard $\Phi' = \Theta$ as *their* scalar potential and $\mathbf{A}^{\parallel'} = \mathbf{C}^{\parallel}$ as the irrotational piece of *their* magnetic vector potential $\mathbf{A}' = \mathbf{C}$. The performance of a gauge transformation by this other party, which changes Φ' and $\mathbf{A}^{\parallel'}$ in general, then coincides with a transformation of Θ and \mathbf{C}^{\parallel} of the form seen in (2.7), seemingly necessitating the existence of this freedom. Although they are not directly observable, \mathbf{A}^{\perp} and \mathbf{C}^{\perp} are uniquely defined and we can, therefore, ascribe a certain physical significance to them; one that is lacked by Φ , \mathbf{A}^{\parallel} , Θ and \mathbf{C}^{\parallel} ¹. Given their privileged status, we refer to \mathbf{A}^{\perp} and \mathbf{C}^{\perp} simply as the ‘first potential’ and the ‘second potential’. In terms of \mathbf{A}^{\perp} and \mathbf{C}^{\perp} , the definitions seen in (2.2) and (2.3) are

$$\begin{aligned}\mathbf{E} &= -\dot{\mathbf{A}}^{\perp} \\ &= -\nabla \times \mathbf{C}^{\perp},\end{aligned}\tag{2.9}$$

$$\begin{aligned}\mathbf{B} &= \nabla \times \mathbf{A}^{\perp} \\ &= -\dot{\mathbf{C}}^{\perp},\end{aligned}\tag{2.10}$$

whilst

$$0 = -\nabla \Phi - \dot{\mathbf{A}}^{\parallel},\tag{2.11}$$

$$0 = -\nabla \Theta - \dot{\mathbf{C}}^{\parallel}.\tag{2.12}$$

Looking at (2.9) and (2.10), we recognise that

$$\nabla \cdot \mathbf{A}^{\perp} = 0,\tag{2.13}$$

$$\nabla \cdot \mathbf{C}^{\perp} = 0,\tag{2.14}$$

$$\nabla \times \mathbf{A}^{\perp} = -\dot{\mathbf{C}}^{\perp},\tag{2.15}$$

$$\nabla \times \mathbf{C}^{\perp} = \dot{\mathbf{A}}^{\perp}.\tag{2.16}$$

These equations (2.13)-(2.16) are identical *in form* to Maxwell’s equations as written in the strict absence of charge (1.68)-(1.71) and also retain this form under a Heaviside-Larmor rotation (2.1). In terms of \mathbf{A}^{\perp} and \mathbf{C}^{\perp} in particular, this is invoked by taking

$$\begin{aligned}\mathbf{A}^{\perp} &\rightarrow \mathbf{A}^{\perp} \cos \theta + \mathbf{C}^{\perp} \sin \theta \\ \mathbf{C}^{\perp} &\rightarrow \mathbf{C}^{\perp} \cos \theta - \mathbf{A}^{\perp} \sin \theta,\end{aligned}\tag{2.17}$$

as was pointed out by Barnett [44, 45]. This self-similarity reccurs indefinitely, in fact, as we delve further into the realms of various integrals of \mathbf{E} and \mathbf{B} and also, as we ascend into the realms of various derivatives of \mathbf{E} and \mathbf{B} . To illustrate the latter, let us define a pseudovector field $\mathbf{G} =$

¹ Indeed, it is permissible to set Φ , \mathbf{A}^{\parallel} , Θ and \mathbf{C}^{\parallel} equal to *zero* if desired, corresponding, in essence, to the choice of the Coulomb gauge (1.14) for $\mathbf{A} = \mathbf{A}^{\perp}$ and the analogous condition $\nabla \cdot \mathbf{C} = 0$ for $\mathbf{C} = \mathbf{C}^{\perp}$.

$\nabla \times \mathbf{E} = -\dot{\mathbf{B}}$ and a vector field $\mathbf{M} = \nabla \times \mathbf{B} = \dot{\mathbf{E}}$. We then find that

$$\nabla \cdot \mathbf{G} = 0, \quad (2.18)$$

$$\nabla \cdot \mathbf{M} = 0, \quad (2.19)$$

$$\nabla \times \mathbf{G} = -\dot{\mathbf{M}}, \quad (2.20)$$

$$\nabla \times \mathbf{M} = \dot{\mathbf{G}}. \quad (2.21)$$

These equations (2.18)-(2.21) are again identical *in form* to Maxwell's equations as written in the strict absence of charge (1.68)-(1.71), as claimed.

2.3 In the presence of charge

We now demonstrate how the results introduced in §2.2 can be generalised to account for the presence of charge.

Electric-magnetic democracy is *not* exhibited by the full set of Maxwell's equations (1.4)-(1.7): it is broken by the presence of charge. It remains possible, of course, to define a scalar potential Φ and a magnetic vector potential \mathbf{A} in the manner indicated in (1.8) and (1.9) as well as by the first equality signs in (2.2) and (2.3) and the first equality signs in (2.4) and (2.5). In contrast, however, the definition of a pseudoscalar potential Θ and an electric pseudovector potential \mathbf{C} in the manner indicated by the second equality signs in (2.2) and (2.3) as well as by the second equality signs in (2.4) and (2.5) is no longer appropriate. In particular, we cannot simply define the second potential \mathbf{C}^\perp in terms of the electric field \mathbf{E} as $\mathbf{E} = -\nabla \times \mathbf{C}^\perp$, as this would contradict Gauss's law² (1.4). Thus, we seek more subtle definitions of Θ and \mathbf{C} here; ones that should then *reduce*, in the strict absence of charge, to those introduced in §2.2. Immediately, however, we recognise *several* possible definitions of \mathbf{C}^\perp that reduce, in the strict absence of charge, to that introduced in §2.2: are we to define \mathbf{C}^\perp in terms of the solenoidal piece \mathbf{E}^\perp of \mathbf{E} as $\mathbf{E}^\perp = -\nabla \times \mathbf{C}^\perp$, for example, or is a (non-equivalent) definition in terms of the magnetic flux density \mathbf{B} such as $\mathbf{B} = -\dot{\mathbf{C}}^\perp$ say, more natural?

In order to proceed concretely, we turn to the normal variables $\tilde{\alpha}$. In the strict absence of charge, \mathbf{C}^\perp depends upon the $\tilde{\alpha}$ as

$$\mathbf{C}^\perp = \iiint_{\infty} \frac{1}{4\sqrt{\pi^3}|\mathbf{k}|^3} \mathbf{k} \times [\tilde{\alpha} \exp(i\mathbf{k} \cdot \mathbf{r}) + \tilde{\alpha}^* \exp(-i\mathbf{k} \cdot \mathbf{r})] d^3\mathbf{k}. \quad (2.22)$$

It seems natural, perhaps, to adopt this as our definition of \mathbf{C}^\perp *in general*. Doing so, we find that

$$\mathbf{E}^\perp = -\nabla \times \mathbf{C}^\perp. \quad (2.23)$$

²The presence of even *one* point charge somewhere in the universe formally prevents us from regarding \mathbf{E} as being solenoidal [11], thus necessitating the careful treatment given in the present section.

Thus, \mathbf{C}^\perp is to \mathbf{E}^\perp what the solenoidal piece \mathbf{A}^\perp of \mathbf{A} is to \mathbf{B} . Furthermore, we find that

$$\begin{aligned}\mathbf{B} &= \iiint_{\infty} \frac{\mathbf{J}(\mathbf{r}', t) \times (\mathbf{r} - \mathbf{r}')}{4\pi|\mathbf{r} - \mathbf{r}'|^3} d^3\mathbf{r}' - \dot{\mathbf{C}}^\perp \\ &= \sum_{n=1}^N \dot{\mathbf{r}}_n \times \frac{q_n(\mathbf{r} - \mathbf{r}_n)}{4\pi|\mathbf{r} - \mathbf{r}_n|^3} - \dot{\mathbf{C}}^\perp.\end{aligned}\quad (2.24)$$

The first term seen on the right-hand side of (2.24) is the non-retarded Biot-Savart law familiar, perhaps, from magnetostatics [2, 3, 9]. Evidently then, the negative of the partial derivative of \mathbf{C}^\perp with respect to time t accounts for deviations in \mathbf{B} from the non-retarded Biot-Savart law. In fact, \mathbf{C}^\perp obeys

$$\begin{aligned}\left(\nabla^2 - \frac{\partial^2}{\partial t^2}\right) \mathbf{C}^\perp &= -\frac{\partial}{\partial t} \iiint_{\infty} \frac{\mathbf{J}(\mathbf{r}', t) \times (\mathbf{r} - \mathbf{r}')}{4\pi|\mathbf{r} - \mathbf{r}'|^3} d^3\mathbf{r}' \\ &= -\frac{\partial}{\partial t} \sum_{n=1}^N \dot{\mathbf{r}}_n \times \frac{q_n(\mathbf{r} - \mathbf{r}_n)}{4\pi|\mathbf{r} - \mathbf{r}_n|^3}.\end{aligned}\quad (2.25)$$

In this wave equation (2.25), the partial derivative with respect to t of the non-retarded Biot-Savart law appears as a source. This seems reasonable in as much as a temporal deviation in the motion of charge away from motion of a magnetostatic character will, in general, give rise to a propagating electromagnetic disturbance with which \mathbf{C}^\perp , being a quantity of particular relevance to the *radiation* field, is associated. Of course, the definitions seen in (2.23) and (2.24) reduce, in the strict absence of charge, to those seen on the second lines of (2.9) and (2.10) as well as on the second lines of (2.4) and (2.5), as desired.

We ‘complete’ our picture now in a simple manner by defining Θ and the irrotational piece \mathbf{C}^\parallel of \mathbf{C} just as we would in the strict absence of charge. That is, as seen in (2.12) so that Θ and \mathbf{C}^\parallel are to the (vanishing) irrotational piece \mathbf{B}^\parallel of \mathbf{B} what Φ and the irrotational piece \mathbf{A}^\parallel of \mathbf{A} are to the irrotational piece \mathbf{E}^\parallel of \mathbf{E} . In the presence of charge, the fact remains that Θ and \mathbf{C}^\parallel are not uniquely defined and both can even be set equal to zero, if desired. In any case, we now have

$$\mathbf{E}^\perp = -\nabla \times \mathbf{C}, \quad (2.26)$$

$$\begin{aligned}\mathbf{B} &= \iiint_{\infty} \frac{\mathbf{J}(\mathbf{r}', t) \times (\mathbf{r} - \mathbf{r}')}{4\pi|\mathbf{r} - \mathbf{r}'|^3} d^3\mathbf{r}' - \nabla\Theta - \dot{\mathbf{C}} \\ &= \sum_{n=1}^N \dot{\mathbf{r}}_n \times \frac{q_n(\mathbf{r} - \mathbf{r}_n)}{4\pi|\mathbf{r} - \mathbf{r}_n|^3} - \nabla\Theta - \dot{\mathbf{C}},\end{aligned}\quad (2.27)$$

in general³. Of course, the definitions seen in (2.26) and (2.27) reduce, in the strict absence of charge, to those seen on the second lines of (2.2) and (2.3), as desired.

Let us now briefly explore the quantum domain in the presence of charge, wherein the operator

³It seems that we *cannot* construct a four-pseudovector from Θ and \mathbf{C} , in contrast to the situation in the strict absence of charge.

$\hat{\mathbf{C}}^\perp = \hat{\mathbf{C}}^\perp(\mathbf{r})$ representing \mathbf{C}^\perp is

$$\hat{\mathbf{C}}^\perp = \sum_{\mathbf{k}} \sqrt{\frac{\hbar}{2|\mathbf{k}|^3 V}} \mathbf{k} \times \left[\hat{\mathbf{a}}_{\mathbf{k}} \exp(i\mathbf{k} \cdot \mathbf{r}) + \hat{\mathbf{a}}_{\mathbf{k}}^\dagger \exp(-i\mathbf{k} \cdot \mathbf{r}) \right]. \quad (2.28)$$

It is interesting, perhaps, to probe the inherently quantum-mechanical characteristics of \mathbf{C}^\perp by evaluating various equal-time commutation relations for its components $\hat{C}_{(a)}^\perp$. We find, for example, that these commute with each other and with the components $\hat{E}_{(a)}^\perp$ of the operator $\hat{\mathbf{E}}^\perp$ representing \mathbf{E}^\perp :

$$\left[\hat{C}_{(a)}^\perp(\mathbf{r}), \hat{C}_{(b)}^\perp(\mathbf{r}') \right] = 0 \quad \left(\text{cf } \left[\hat{A}_{(a)}^\perp(\mathbf{r}), \hat{A}_{(b)}^\perp(\mathbf{r}') \right] = 0 \right), \quad (2.29)$$

$$\left[\hat{C}_{(a)}^\perp(\mathbf{r}), \hat{E}_{(b)}^\perp(\mathbf{r}') \right] = 0 \quad \left(\text{cf } \left[\hat{A}_{(a)}^\perp(\mathbf{r}), \hat{B}_{(b)}^\perp(\mathbf{r}') \right] = 0 \right). \quad (2.30)$$

These commutation relations (2.29) and (2.30) mirror the well-established analogous equal-time commutation relations for the components $\hat{A}_{(a)}^\perp$ of the operator $\hat{\mathbf{A}}^\perp$ representing the first potential \mathbf{A}^\perp , as indicated [11, 12]. A given component of $\hat{\mathbf{C}}^\perp$ commutes with the same component of $\hat{\mathbf{A}}^\perp$ but *not* with the two orthogonal components of $\hat{\mathbf{A}}^\perp$ or with the components $\hat{B}_{(a)}^\perp$ of the operator $\hat{\mathbf{B}}$ representing \mathbf{B} , as

$$\left[\hat{C}_{(a)}^\perp(\mathbf{r}), \hat{A}_{(b)}^\perp(\mathbf{r}') \right] = - \int \int \int_{\infty} \frac{\hbar \epsilon_{(abc)} \hat{k}_{(c)}}{8\pi^3 |\mathbf{k}|} \exp[i\mathbf{k} \cdot (\mathbf{r} - \mathbf{r}')] d^3\mathbf{k} \quad (2.31)$$

$$= - \frac{i\hbar \epsilon_{(abc)} (\mathbf{r} - \mathbf{r}')_{(c)}}{4\pi |\mathbf{r} - \mathbf{r}'|^3},$$

$$\left[\hat{C}_{(a)}^\perp(\mathbf{r}), \hat{B}_{(b)}^\perp(\mathbf{r}') \right] = - \int \int \int_{\infty} \frac{i\hbar}{8\pi^3} \left[\delta_{(ab)} - \hat{k}_{(a)} \hat{k}_{(b)} \right] \exp[i\mathbf{k} \cdot (\mathbf{r} - \mathbf{r}')] d^3\mathbf{k} \quad (2.32)$$

$$= -i\hbar \delta_{(ab)}^\perp(\mathbf{r} - \mathbf{r}') \quad \left(\text{cf } \left[\hat{A}_{(a)}^\perp(\mathbf{r}), \hat{E}_{(b)}^\perp(\mathbf{r}') \right] = -i\hbar \delta_{(ab)}^\perp(\mathbf{r} - \mathbf{r}') \right).$$

The first commutation relation (2.31) above may be thought of as underlying the well established [11–13] equal-time commutation relation between the $\hat{E}_{(a)}^\perp$ and the $\hat{B}_{(a)}^\perp$. The second commutation relation (2.32) above mirrors the well-established [11–13] analogous equal-time commutation relation for the $\hat{A}_{(a)}^\perp$, as indicated.

2.4 Discussion

We have reviewed and examined the introduction of a pseudoscalar potential Θ and an electric pseudovector potential \mathbf{C} in the strict *absence* of charge which led us in particular to identify a remarkable self-similarity then inherent to Maxwell's equations (1.68)-(1.71). In addition, we have suggested meaningful definitions of Θ and \mathbf{C} in the *presence* of charge. The focus of our attention has been the second potential \mathbf{C}^\perp , for this quantity makes explicit and seemingly natural appearances in the fundamental description of the angular momentum of light, as we will see in §3. It might be instructive, however, to investigate Θ and the irrotational piece \mathbf{C}^\parallel of \mathbf{C} in more detail. This is a task for future research.

Chapter 3

The Angular Momentum of Light

3.1 Introduction

Light possesses mechanical properties, some of which are familiar, perhaps, from our everyday experiences: the energy radiated by a light bulb can be employed to drive the solar cell of a pocket calculator whilst that transported by a laser beam enables the cutting of metal or the obliteration of cancer cells; the linear momentum carried by sunlight is partly responsible for a comet's tail¹ and prevents the sun itself from collapsing under its own weight [36]. Less familiar from our everyday experiences, however, is the fact that light possesses *angular* momentum.

The study of the angular momentum of light began, it seems, with the work of Poynting [47], who inferred by analogy with a revolving cylindrical shaft that a beam of circularly polarised light possesses an intrinsic rotation angular momentum in the direction of propagation equivalent to $\pm\hbar$ per photon, the plus and minus signs corresponding to left- and right-handed circular polarisation. The existence of this so-called spin was confirmed in experiment by Beth [48], who measured the torque experienced by a half wave plate as the plate changed the spin of light passing through it. The rotation angular momentum of light that is not spin is referred to instead as orbital angular momentum and might be thought to be rather trivial and purely extrinsic. Pursuing an analogy between paraxial optics and the quantum harmonic oscillator, Allen, Beijersbergen, Spreeuw and Woerdman made the discovery, however, that a Laguerre-Gaussian beam of light possesses a well defined orbital angular momentum equivalent to $\hbar\ell$ per photon in the direction of propagation by virtue of possessing helical phase fronts of winding number $\ell \in \{0, \pm 1, \dots\}$ [49]. This orbital angular momentum is, in fact, intrinsic, as was pointed out by Berry [50]. The use of the spin and / or orbital angular momentum of light to rotate material bodies about their centres and / or about a beam axis has been amply demonstrated and a wealth of additional applications for the angular momentum of light have been recognised and pursued besides [26, 46, 51].

Surprisingly, perhaps, the fundamental description of the angular momentum of light in the theory of electrodynamics brings with it many subtleties and has been the source of much controversy. It is with this subject that the present chapter is concerned. We explain in particular that light possesses

¹This was suggested by Keppler [46].

an *infinite* number of distinct angular momenta, in addition to spin and orbital angular momentum. The text is based primarily upon my research papers [37], [52] and [53]. Initially, we consider light that is propagating freely in the strict absence of charge. Maxwell's equations (1.4)-(1.7) then reduce to

$$\begin{aligned}\nabla \cdot \mathbf{E} &= 0, \\ \nabla \cdot \mathbf{B} &= 0, \\ \nabla \times \mathbf{E} &= -\dot{\mathbf{B}}, \\ \nabla \times \mathbf{B} &= \dot{\mathbf{E}},\end{aligned}$$

as seen also in (1.68)-(1.71). We will subsequently generalise our findings, in §3.7, to account for the presence of charge.

3.2 Review of previously established results

As a precursor to the original research described in §3.3-§3.8, let us begin by reviewing some pertinent results that were already established at the time of starting my doctoral research.

A fair starting point, perhaps, for an investigation into the angular momentum of light is Poynting's vector [54]

$$\mathbf{g} = \mathbf{E} \times \mathbf{B} \quad (3.1)$$

which can be regarded as a linear momentum density as it yields the linear momentum [2, 8, 11]

$$\mathcal{G} = \iiint_{\infty} \mathbf{E} \times \mathbf{B} \, d^3\mathbf{r} \quad (3.2)$$

when integrated over all space; the operator $\hat{\mathcal{G}}$ representing \mathcal{G} being the generator in turn of translations in space. We might then construct a density \mathbf{j} of rotation angular momentum about the origin $\mathbf{r} = 0$ by taking the cross product of position \mathbf{r} with \mathbf{g} as

$$\mathbf{j} = \mathbf{r} \times (\mathbf{E} \times \mathbf{B}), \quad (3.3)$$

if only by analogy with mechanics. This identification is indeed justified as \mathbf{j} yields the rotation angular momentum [2, 8, 11]

$$\mathcal{J} = \iiint_{\infty} \mathbf{r} \times (\mathbf{E} \times \mathbf{B}) \, d^3\mathbf{r} \quad (3.4)$$

when integrated over all space; the operator $\hat{\mathcal{J}}$ representing \mathcal{J} being the generator in turn of circular rotations in space. Making use of an integration by parts, \mathcal{J} can be separated into two distinct pieces as

$$\mathcal{J} = \iiint_{\infty} \mathbf{E} \times \mathbf{A}^{\perp} \, d^3\mathbf{r} + \iiint_{\infty} E_{(a)} (\mathbf{r} \times \nabla) A_{(a)}^{\perp} \, d^3\mathbf{r}, \quad (3.5)$$

an observation due to Darwin [24, 55] and Humblet [56, 57]. This separation is gauge invariant. The first piece

$$\begin{aligned}\mathcal{S} &= \int \int \int_{\infty} \mathbf{E} \times \mathbf{A}^{\perp} d^3\mathbf{r} \\ &= \int \int \int_{\infty} i\tilde{\alpha} \times \tilde{\alpha}^* d^3\mathbf{k}\end{aligned}\quad (3.6)$$

is intrinsic and may be identified, therefore, as the spin \mathcal{S} , as is indicated. Indeed, a close analogy can be drawn between the form seen on the second line of (3.6) and that expected of a spin-one particle (the photon) of vector wavefunction $\tilde{\alpha}$ in reciprocal space, as is elucidated in the book by Cohen-Tannoudji, Dupont-Roc and Grynberg [11], for example. The operator

$$\begin{aligned}\hat{\mathcal{S}} &= \int \int \int_V \hat{\mathbf{E}} \times \hat{\mathbf{A}}^{\perp} d^3\mathbf{r} \\ &= \sum_{\mathbf{k}} \sum_{\sigma} \sigma \hbar \mathbf{k} \hat{n}_{\mathbf{k}\sigma}\end{aligned}\quad (3.7)$$

representing \mathcal{S} describes a spin of $\pm \hbar \hat{\mathbf{k}}$ per circularly polarised plane-wave-mode photon of wavevector \mathbf{k} and polarisation parameter $\sigma = \pm 1$, as was observed by Lenstra and Mandel [58]. This is in line, of course, with Poynting's inference [47] and the observations of Beth [48]. $\hat{\mathcal{S}}$ is the generator of the closest approximation to a rotation of the orientations of the electric field vectors and magnetic flux density pseudovectors that is consistent with the requirement that they retain their solenoidal character, an observation due to van Enk and Nienhuis [59, 60] and Barnett [44]. The second piece

$$\begin{aligned}\mathcal{L} &= \int \int \int_{\infty} E_{(a)} (\mathbf{r} \times \nabla) A_{(a)}^{\perp} d^3\mathbf{r} \\ &= \int \int \int_{\infty} i\tilde{\alpha}_{(a)} (\mathbf{k} \times \nabla_{\mathbf{k}}) \tilde{\alpha}_{(a)}^* d^3\mathbf{k},\end{aligned}\quad (3.8)$$

with $\nabla_{\mathbf{k}}$ the gradient operator with respect to \mathbf{k} , is explicitly dependent upon \mathbf{r} and may be identified as the orbital angular momentum \mathcal{L} , as is indicated. The two components of \mathcal{L} that are orthogonal to \mathcal{G} are extrinsic whilst that parallel to \mathcal{G} can be non-vanishing and is intrinsic, as was pointed out by Berry [50]. The operator $\hat{\mathcal{L}}$ representing \mathcal{L} is the generator of the closest approximation to a rotation of the spatial distribution of the light that is consistent with the requirement that the light retains its solenoidal character, an observation due to Barnett [44]. For additional perspectives on the separation of \mathcal{J} into \mathcal{S} and \mathcal{L} , see [55, 61], for example.

It was pointed out by van Enk and Nienhus [59, 60] that the components of $\hat{\mathcal{S}}$ commute with each other. Thus, unlike $\hat{\mathcal{J}}$, neither $\hat{\mathcal{S}}$ nor $\hat{\mathcal{L}}$ separately obey the usual angular momentum commutation relations (1.161). For this reason, it is often said that \mathcal{S} and \mathcal{L} are not 'true' angular momenta.

A further advancement in the study of \mathcal{S} and \mathcal{L} was made recently by Barnett [44], who observed that

the integrands $\mathbf{E} \times \mathbf{A}^\perp$ and $E_{(a)} (\mathbf{r} \times \nabla) A_{(a)}^\perp$ of \mathcal{S} and \mathcal{L} seen on the first lines of (3.6) and (3.8) do not obviously retain their form under a Heaviside-Larmor rotation (2.1) and thus, do not obviously reflect the electric-magnetic symmetry inherent to Maxwell's equations as written in the strict absence of charge (1.68)-(1.71). He explained, however, that \mathcal{S} and \mathcal{L} may be expressed equivalently as

$$\begin{aligned}\mathcal{S} &= \iiint_{\infty} \mathbf{E} \times \mathbf{A}^\perp d^3\mathbf{r} \\ &= \iiint_{\infty} \frac{1}{2} (\mathbf{E} \times \mathbf{A}^\perp + \mathbf{B} \times \mathbf{C}^\perp) d^3\mathbf{r},\end{aligned}\tag{3.9}$$

$$\begin{aligned}\mathcal{L} &= \iiint_{\infty} E_{(a)} (\mathbf{r} \times \nabla) A_{(a)}^\perp d^3\mathbf{r} \\ &= \iiint_{\infty} \frac{1}{2} [E_{(a)} (\mathbf{r} \times \nabla) A_{(a)}^\perp + B_{(a)} (\mathbf{r} \times \nabla) C_{(a)}^\perp] d^3\mathbf{r}.\end{aligned}\tag{3.10}$$

The forms seen on the second lines of (3.9) and (3.10), in particular the integrands, *are* manifestly invariant under a Heaviside-Larmor rotation (2.1), which led Barnett to propose

$$\mathbf{s} = \frac{1}{2} (\mathbf{E} \times \mathbf{A}^\perp + \mathbf{B} \times \mathbf{C}^\perp),\tag{3.11}$$

$$\mathbf{l} = \frac{1}{2} [E_{(a)} (\mathbf{r} \times \nabla) A_{(a)}^\perp + B_{(a)} (\mathbf{r} \times \nabla) C_{(a)}^\perp],\tag{3.12}$$

as spin and orbital angular momentum densities.

Let us introduce here the angular momentum tensor [2]

$$M^{\alpha\beta\gamma} = \frac{1}{2} [x^\alpha (F^\beta_\delta F^{\delta\gamma} + G^\beta_\delta G^{\delta\gamma}) - x^\beta (F^\alpha_\delta F^{\delta\gamma} + G^\alpha_\delta G^{\delta\gamma})]\tag{3.13}$$

which, owing to the antisymmetry $M^{\alpha\beta\gamma} = -M^{\beta\alpha\gamma}$, has twenty-four distinct components. The x , y and z components j_x , j_y and j_z of \mathbf{j} appear as the $\alpha\beta\gamma = 230$, 310 and 120 components of $M^{\alpha\beta\gamma}$ and the continuity equation

$$\partial_\gamma M^{\alpha\beta\gamma} = 0\tag{3.14}$$

thus expresses the local conservation of the x , y and z components of rotation angular momentum for $\alpha\beta = 23$, 31 and 12 . It follows, of course, that rotation angular momentum is globally conserved:

$$\dot{\mathcal{J}} = 0.\tag{3.15}$$

That \mathcal{S} and \mathcal{L} , which comprise $\mathcal{J} = \mathcal{S} + \mathcal{L}$, are indeed of distinct character is manifest in the fact that spin and orbital angular momentum are separately globally conserved:

$$\dot{\mathcal{S}} = 0,\tag{3.16}$$

$$\dot{\mathcal{L}} = 0,\tag{3.17}$$

as was observed by van Enk and Nienhuis [59, 60].

Evidently, *rotation* angular momentum constitutes but one half of the angular momentum story, at least as far as the theory of special relativity is concerned: the $\alpha\beta = 01, 02$ and 03 components of (3.14) express the local conservation of the x , y and z components of *boost* angular momentum ‘about’ time $t = 0$ and $\mathbf{r} = 0$. The boost angular momentum

$$\begin{aligned}\mathcal{K} &= \iiint_{\infty} \left[t \mathbf{E} \times \mathbf{B} - \frac{1}{2} \mathbf{r} (\mathbf{E} \cdot \mathbf{E} + \mathbf{B} \cdot \mathbf{B}) \right] d^3\mathbf{r} \\ &= \iiint_{\infty} t \mathbf{k} \tilde{\alpha} \cdot \tilde{\alpha}^* d^3\mathbf{k} + \iiint_{\infty} \frac{i|\mathbf{k}|}{2} \left[\tilde{\alpha}_{(a)} \nabla_{\mathbf{k}} \tilde{\alpha}_{(a)}^* - \tilde{\alpha}_{(a)}^* \nabla_{\mathbf{k}} \tilde{\alpha}_{(a)} \right] d^3\mathbf{k}\end{aligned}\quad (3.18)$$

is obtained by integrating the boost angular momentum density components M^{010} , M^{020} and M^{030} over all space; the operator $\hat{\mathcal{K}}$ representing \mathcal{K} being the generator of boosts. The physical significance of boost angular momentum is best illustrated, perhaps, by considering its global conservation:

$$\dot{\mathcal{K}} = 0, \quad (3.19)$$

which implies that

$$\begin{aligned}\frac{d}{dt} \frac{\iiint_{\infty} \mathbf{r} \frac{1}{2} (\mathbf{E} \cdot \mathbf{E} + \mathbf{B} \cdot \mathbf{B}) d^3\mathbf{r}}{\mathcal{W}} &= \frac{\dot{\mathcal{G}}}{\mathcal{W}} \\ &= \text{constant},\end{aligned}\quad (3.20)$$

where we have divided (3.19) through by the energy

$$\mathcal{W} = \iiint_{\infty} \frac{1}{2} (\mathbf{E} \cdot \mathbf{E} + \mathbf{B} \cdot \mathbf{B}) d^3\mathbf{r} \quad (3.21)$$

and made use of the global conservation of energy and the global conservation of linear momentum:

$$\dot{\mathcal{W}} = 0, \quad (3.22)$$

$$\dot{\mathcal{G}} = 0. \quad (3.23)$$

This (3.20) may be regarded as a statement of the uniform motion of the postion

$$\frac{\iiint_{\infty} \mathbf{r} \frac{1}{2} (\mathbf{E} \cdot \mathbf{E} + \mathbf{B} \cdot \mathbf{B}) d^3\mathbf{r}}{\mathcal{W}} \quad (3.24)$$

of the centre of energy [10]. The question was posed recently by Barnett [45]: is it possible to separate \mathcal{K} into ‘spin’ and ‘orbital’ contributions, in analogy with the separation of \mathcal{J} into \mathcal{S} and \mathcal{L} . To this end, he observed that \mathcal{K} can be recast using integration by parts, in a gauge-invariant manner, as

$$\mathcal{K} = \mathcal{V} + \mathcal{Y} \quad (3.25)$$

with

$$\mathcal{V} = \iiint_{\infty} \frac{1}{2} \left(-\mathbf{E} \times \mathbf{C}^{\perp} + \mathbf{B} \times \mathbf{A}^{\perp} \right) d^3\mathbf{r}, \quad (3.26)$$

which does not make explicit reference to t or \mathbf{r} , and

$$\mathcal{V} = \iiint_{\infty} \frac{1}{2} \left[-A_{(a)}^{\perp} \left(t \nabla + \mathbf{r} \frac{\partial}{\partial t} \right) E_{(a)} - C_{(a)}^{\perp} \left(t \nabla + \mathbf{r} \frac{\partial}{\partial t} \right) B_{(a)} \right] d^3\mathbf{r}, \quad (3.27)$$

which does make explicit reference to t and \mathbf{r} . It is natural, perhaps, to identify \mathcal{V} as boost spin and \mathcal{Y} as boost orbital angular momentum. This separation fails, however, in that \mathcal{V} vanishes ($\mathcal{V} = 0$) and so $\mathcal{K} = \mathcal{Y}$ [45].

3.3 Intrinsic rotation angular momenta

The starting point for our investigation into the angular momentum of light is the observation due to van Enk and Nienhuis [59, 60] and discussed in §3.2 that the operator $\hat{\mathcal{S}}$ representing the spin \mathcal{S} does not obey the usual angular momentum commutation relations (1.161). Although this may be surprising at first glance and is sometimes reported as being paradoxical, it may be understood or at least appreciated by recalling a concept familiar from particle physics: the photon is massless and relativity suggests, therefore, that the photon only possesses *one* well defined component of spin; the component in the direction of propagation [59, 60, 62]. This is apparent, in fact, on the second line of (3.7). The value taken by this component of spin relative to the direction of propagation is referred to as the photon's *helicity* [8, 59, 60, 62, 63].

3.3.1 Helicity

We begin now with a search for the explicit form taken by the helicity \mathcal{H} . We are guided by our observation that \mathcal{H} must be an intrinsic time-even conserved Lorentz pseudoscalar with the dimensions of a rotation angular momentum.

In particle physics, the single-particle helicity is the expectation value of the helicity operator

$$\hat{\Sigma} \cdot \frac{\hat{\mathbf{p}}}{|\hat{\mathbf{p}}|}, \quad (3.28)$$

which is the scalar product of the spin operator $\hat{\Sigma}$ with the normalised linear momentum operator $\hat{\mathbf{p}}/|\hat{\mathbf{p}}|$. It seems natural, perhaps, to try and determine \mathcal{H} using this definition, but we then run into difficulties with the form of the photon wavefunction [11]. We can certainly attempt to use the electric field \mathbf{E} and the magnetic flux density \mathbf{B} as the basis of a photon wavefunction via the Riemann-Silberstein field $\tilde{\mathbf{F}} = (\mathbf{E} + i\mathbf{B})/\sqrt{2}$, but the resulting quantity does not possess the dimensions of a rotation angular momentum [63]. A time-even pseudoscalar with the dimensions of a rotation angular momentum has, however, already been recognised in plasma physics for some time: the magnetic

helicity²

$$\mathcal{H}_M = \iiint \mathbf{A} \cdot \mathbf{B} d^3\mathbf{r} \quad (3.29)$$

was introduced by Wotjier to understand relaxation processes in plasmas [65] and is often employed to quantify the twist of magnetic flux density lines [66, 67]. \mathcal{H}_M is gauge invariant provided the boundary of the region of integration is chosen appropriately, despite the explicit appearance of a magnetic vector potential \mathbf{A} ³. It formally resembles the ‘vortex helicity’ or ‘fluid helicity’

$$\mathcal{V} = \iiint \mathbf{u} \cdot (\nabla \times \mathbf{u}) d^3\mathbf{r} \quad (3.30)$$

introduced by Moreau [68], with $\mathbf{u} = \mathbf{u}(\mathbf{r}, t)$ the fluid velocity field. Unfortunately, our search is not yet over: \mathcal{H}_M is *not* the quantity we seek. In particular, \mathcal{H}_M is neither conserved nor Lorentz invariant.

To proceed, we follow the approach taken by Barnett [44, 45] and observe that \mathcal{H}_M does not retain its form under a Heaviside-Larmor rotation (2.1). If, however, we add half of \mathcal{H}_M to half of an analogous electric helicity, we obtain

$$\begin{aligned} \mathcal{H} &= \iiint_{\infty} \frac{1}{2} (\mathbf{A}^{\perp} \cdot \mathbf{B} - \mathbf{C}^{\perp} \cdot \mathbf{E}) d^3\mathbf{r} \\ &= \iiint_{\infty} i\tilde{\alpha} \times \tilde{\alpha}^* \cdot \hat{\mathbf{k}} d^3\mathbf{k}, \end{aligned} \quad (3.31)$$

which does retain its form under a Heaviside-Larmor rotation (2.1) and is, in fact, the quantity that we seek, as is indicated. The operator

$$\begin{aligned} \hat{\mathcal{H}} &= \iiint_V \frac{1}{2} (\hat{\mathbf{A}}^{\perp} \cdot \hat{\mathbf{B}} - \hat{\mathbf{C}}^{\perp} \cdot \hat{\mathbf{E}}) d^3\mathbf{r} \\ &= \sum_{\mathbf{k}} \sum_{\sigma} \sigma \hbar \hat{n}_{\mathbf{k}\sigma} \end{aligned} \quad (3.32)$$

representing \mathcal{H} describes a helicity of $\pm\hbar$ per circularly polarised plane-wave-mode photon of wavevector \mathbf{k} and polarisation parameter $\sigma = \pm 1$. This is in line, of course, with the concept of helicity familiar from particle physics [8, 59, 60, 62, 63]. The global conservation of helicity

$$\dot{\mathcal{H}} = 0 \quad (3.33)$$

may be readily confirmed. Looking at the integrand of \mathcal{H} seen on the first line of (3.31), we identify

$$h = \frac{1}{2} (\mathbf{A}^{\perp} \cdot \mathbf{B} - \mathbf{C}^{\perp} \cdot \mathbf{E}), \quad (3.34)$$

as a helicity density.

²The use of the word ‘helicity’ in this context is due to Moffatt [64] who proposed it by analogy with the concept of helicity familiar to him from particle physics.

³Indeed, one can in such cases replace \mathbf{A} with \mathbf{A}^{\perp} as \mathbf{A}^{\parallel} makes no contribution to \mathcal{H}_M .

To the best of our knowledge, \mathcal{H} was first recognised by Candlin [69], who referred to it as the ‘screw action’. It has since been rediscovered and investigated in a variety of contexts outwith the angular momentum of light [6, 43, 70–77].

By virtue of the equalities linking the first and second lines of (3.9) and of (3.10), it might be argued that the explicit acknowledgement of the second potential \mathbf{C}^\perp in addition to the first potential \mathbf{A}^\perp in the spin \mathcal{S} and orbital angular momentum \mathcal{L} is not necessary but rather, is something of a matter of taste. It should be noted, however, that the appearance of \mathbf{C}^\perp in \mathcal{H} is seemingly inescapable: there is no equality relating the magnetic and electric pieces of \mathcal{H} in general and both must be present, thus bolstering Barnett’s suggestion that \mathbf{C}^\perp is just as important as \mathbf{A}^\perp in the fundamental description of the angular momentum of light [44, 45].

3.3.2 Spin

Although they are closely related, helicity and spin are ultimately distinct and should not be confused. Whilst both are intrinsic, conserved and possess the dimensions of a rotation angular momentum, \mathcal{H} is a time-even Lorentz pseudoscalar whereas \mathcal{S} is a time-odd pseudovector. For ease of comparison, we summarise here those results presented in §3.2 for spin that are analogous to those presented in §3.3.1 for helicity.

The spin is

$$\begin{aligned}\mathcal{S} &= \iiint_{\infty} \frac{1}{2} \left(\mathbf{E} \times \mathbf{A}^\perp + \mathbf{B} \times \mathbf{C}^\perp \right) d^3\mathbf{r} \\ &= \iiint_{\infty} i\tilde{\alpha} \times \tilde{\alpha}^* d^3\mathbf{k}\end{aligned}$$

and is represented by the operator

$$\begin{aligned}\hat{\mathcal{S}} &= \iiint_V \frac{1}{2} \left(\hat{\mathbf{E}} \times \hat{\mathbf{A}}^\perp + \hat{\mathbf{B}} \times \hat{\mathbf{C}}^\perp \right) d^3\mathbf{r} \\ &= \sum_{\mathbf{k}} \sum_{\sigma} \sigma \hbar \hat{\mathbf{k}} \hat{n}_{\mathbf{k}\sigma}\end{aligned}$$

which describes a spin of $\pm \hbar \hat{\mathbf{k}}$ per circularly polarised plane-wave-mode photon of wavevector \mathbf{k} and polarisation parameter $\sigma = \pm 1$: if you like, helicity $\pm \hbar$ with a sense of the direction $\hat{\mathbf{k}}$. Spin is globally conserved:

$$\dot{\mathcal{S}} = 0,$$

and we can identify

$$\mathbf{s} = \frac{1}{2} \left(\mathbf{E} \times \mathbf{A}^\perp + \mathbf{B} \times \mathbf{C}^\perp \right)$$

as a spin density.

3.3.3 The ab infra zilches

Helicity and the components of spin are not the only intrinsic rotation angular momenta. We recognise here a further six intrinsic rotation angular momenta which we refer to as the ab infra zilches in homage to the ab zilches, due to Lipkin [78] and discussed in §3.4, which are similar in form.

The ab infra zilches $\mathcal{N}_{(ab)}$ comprise a time-even rotational pseudotensor of rank two, being

$$\begin{aligned}\mathcal{N}_{(ab)} &= \int \int \int_{\infty} \frac{1}{2} \left[\delta_{(ab)} \left(\mathbf{A}^{\perp} \cdot \mathbf{B} - \mathbf{C}^{\perp} \cdot \mathbf{E} \right) - A_{(a)}^{\perp} B_{(b)} - A_{(b)}^{\perp} B_{(a)} + C_{(a)}^{\perp} E_{(b)} + C_{(b)}^{\perp} E_{(a)} \right] d^3 \mathbf{r} \\ &= \int \int \int_{\infty} i \tilde{\boldsymbol{\alpha}} \times \tilde{\boldsymbol{\alpha}}^* \cdot \hat{\mathbf{k}} \hat{k}_{(a)} \hat{k}_{(b)} d^3 \mathbf{k}.\end{aligned}\quad (3.35)$$

The operator

$$\begin{aligned}\hat{\mathcal{N}}_{(ab)} &= \int \int \int_V \frac{1}{2} \left[\delta_{(ab)} \left(\hat{\mathbf{A}}^{\perp} \cdot \hat{\mathbf{B}} - \hat{\mathbf{C}}^{\perp} \cdot \hat{\mathbf{E}} \right) - \hat{A}_{(a)}^{\perp} \hat{B}_{(b)} - \hat{A}_{(b)}^{\perp} \hat{B}_{(a)} + \hat{C}_{(a)}^{\perp} \hat{E}_{(b)} + \hat{C}_{(b)}^{\perp} \hat{E}_{(a)} \right] d^3 \mathbf{r} \\ &= \sum_{\mathbf{k}} \sum_{\sigma} \sigma \hbar \hat{k}_{(a)} \hat{k}_{(b)} \hat{n}_{\mathbf{k}\sigma}\end{aligned}\quad (3.36)$$

representing $\mathcal{N}_{(ab)}$ describes an ab infra zilch of $\pm \hbar \hat{k}_{(a)} \hat{k}_{(b)}$ per circularly polarised plane-wave-mode photon of wavevector \mathbf{k} and polarisation parameter $\sigma = \pm 1$: if you like, helicity $\pm \hbar$ with a simultaneous sense of the directions $\hat{k}_{(a)}$ and $\hat{k}_{(b)}$. Only five of the $\mathcal{N}_{(ab)}$ are actually ‘new’ quantities, as $\mathcal{N}_{(ab)} = \mathcal{N}_{(ba)}$ and $\mathcal{N}_{(aa)} = \mathcal{H}$. The latter may be regarded as a reflection of the fact that $\hat{k}_{(a)} \hat{k}_{(a)} = 1$. The ab infra zilches are globally conserved:

$$\dot{\mathcal{N}}_{(ab)} = 0. \quad (3.37)$$

It follows by virtue of the principle axis theorem that we can always orient our coordinate system such that the xy , xz and yz infra zilches vanish. Looking at the integrand of the $\mathcal{N}_{(ab)}$ seen on the first line of (3.35), we identify

$$n_{(ab)} = \frac{1}{2} \left[\delta_{(ab)} \left(\mathbf{A}^{\perp} \cdot \mathbf{B} - \mathbf{C}^{\perp} \cdot \mathbf{E} \right) - A_{(a)}^{\perp} B_{(b)} - A_{(b)}^{\perp} B_{(a)} + C_{(a)}^{\perp} E_{(b)} + C_{(b)}^{\perp} E_{(a)} \right], \quad (3.38)$$

as an ab infra zilch density.

3.3.4 Ad infinitum

In §3.3.1-§3.3.3, we identified the helicity \mathcal{H} ($\pm \hbar$ per circularly polarised plane-wave-mode photon of wavevector \mathbf{k} and polarisation parameter $\sigma = \pm 1$), the components $\mathcal{S}_{(a)}$ of spin \mathcal{S} ($\pm \hbar \hat{k}_{(a)}$ per photon) and the ab infra zilches $\mathcal{N}_{(ab)}$ ($\pm \hbar \hat{k}_{(a)} \hat{k}_{(b)}$ per photon) as being intrinsic rotation angular momenta. We recognise here that these are but the first three members of an *infinite* collection of intrinsic rotation angular momenta. Although the forms taken by these in ordinary space becomes

increasingly obscure, the forms taken in reciprocal space remain relatively simple, being

$$\int \int \int_{\infty} i \tilde{\alpha} \times \tilde{\alpha}^* \cdot \hat{\mathbf{k}} \overbrace{\hat{k}_{(a)} \hat{k}_{(b)} \hat{k}_{(c)} \dots}^{r \text{ components of } \hat{\mathbf{k}}} d^3 \mathbf{k} \quad (3.39)$$

with associated operators

$$\sum_{\mathbf{k}} \sum_{\sigma} \sigma \hbar \overbrace{\hat{k}_{(a)} \hat{k}_{(b)} \hat{k}_{(c)} \dots}^{r \text{ components of } \hat{\mathbf{k}}} \hat{n}_{\mathbf{k}\sigma} \quad (3.40)$$

which describe intrinsic rotation angular momenta of $\pm \hbar \hat{k}_{(a)} \hat{k}_{(b)} \hat{k}_{(c)} \dots$ per circularly polarised plane-wave-mode photon of wavevector \mathbf{k} and polarisation parameter $\sigma = \pm 1$, where $r \in \{0, 1, \dots\}$: if you like, helicity $\pm \hbar$ with a simultaneous sense of the directions $\hat{k}_{(a)}, \hat{k}_{(b)}, \hat{k}_{(c)}, \dots$. For $r = 0$ we have \mathcal{H} , for $r = 1$ we have the components $\mathcal{S}_{(a)}$ of \mathcal{S} , for $r = 2$ we have the $\mathcal{N}_{(ab)}$ and so on, ad infinitum. This suggests in particular that spin is perhaps most meaningfully thought of as one piece of a larger description of helicity. The forms seen in (3.39) and (3.40) are independent of t . For the remainder of this thesis, we will restrict our attention to helicity, spin and the ab infra zilches with the understanding, of course, that some of the ideas presented can be extended indefinitely.

\mathcal{H} has simple Lorentz transformation properties whereas \mathcal{S} , the $\mathcal{N}_{(ab)}$ etc do not. Thus, \mathcal{S} , the $\mathcal{N}_{(ab)}$ etc may be identified in any frame of reference but are not related simply between different frames of reference, in general. This does not negate their physical significance, however. To give a familiar example; the position (3.24) of the centre of energy can be identified in any frame of reference but is not related simply between different frames of reference, in general. Nevertheless, we recognise it as being a physically significant quantity.

3.3.5 The helicity array

Helicity, spin and the ab infra zilches, whilst being ultimately distinct, are intimately associated. We now demonstrate this through the introduction of the helicity array $N^{\alpha\beta\gamma}$: a rank-three object⁴ with components

$$\begin{aligned} N^{000} &= h, \\ N^{0a0} &= s_{(a)}, \\ N^{ab0} &= n_{(ab)} \end{aligned} \quad (3.41)$$

⁴A helicity array of arbitrarily high rank can be constructed which incorporates as many of the infinite collection of intrinsic rotation angular momenta discussed in §3.3.4 as desired.

and

$$\begin{aligned}
N^{00a} &= N^{0a0}, \\
N^{0ab} &= N^{ab0}, \\
N^{abc} &= \delta_{(ab)}N^{00c} + \frac{1}{2} \left[-A_{(a)}^\perp \partial_c C_{(b)}^\perp - A_{(b)}^\perp \partial_c C_{(a)}^\perp + C_{(a)}^\perp \partial_c A_{(b)}^\perp + C_{(b)}^\perp \partial_c A_{(a)}^\perp \right], \quad (3.42)
\end{aligned}$$

with the symmetry $N^{\alpha\beta\gamma} = N^{\beta\alpha\gamma}$ to be understood in our definitions. Despite its suggestive structure, $N^{\alpha\beta\gamma}$ is *not* a tensor or pseudotensor and no significance is to be placed upon the fact that its indices are seemingly contravariant.

The significance of $N^{\alpha\beta\gamma}$ lies in the fact that it satisfies the continuity equation

$$\partial_\gamma N^{\alpha\beta\gamma} = 0 \quad (3.43)$$

which embodies nine distinct conservation laws.

(i) For $\alpha\beta = 00$, (3.43) is

$$\dot{h} + \nabla \cdot \mathbf{s} = 0, \quad (3.44)$$

which embodies the conservation of helicity. Evidently, \mathbf{s} plays a dual role in that it is simultaneously a spin density and a helicity flux density ($N^{0a0} = N^{00a}$).

(ii) For $\alpha\beta = 0a$, (3.43) is

$$\dot{s}_{(a)} + \partial_b n_{(ab)} = 0, \quad (3.45)$$

which embodies the conservation of spin. Here we see that the $n_{(ab)}$ play dual roles in that they are simultaneously ab infra zilch densities and the components of a spin flux density ($N^{ab0} = N^{0ab}$).

(iii) Finally, for $\alpha\beta = ab$, (3.43) is

$$\dot{n}_{(ab)} + \partial_c N^{abc} = 0, \quad (3.46)$$

which embodies the conservation of the ab infra zilches.

We emphasise that helicity, spin and the ab infra zilches are distinct. Their associated densities; h , \mathbf{s} and $n_{(ab)}$, however, are related by a hierarchy of continuity equations. Loosely speaking, helicity is conserved and is transported by spin, which is itself conserved and is transported by the ab infra zilches, which are themselves conserved and are transported by the N^{abc} . This hierarchy is reminiscent of that found in the description of energy and linear momentum, where it is well known [2, 3] that energy is conserved and is transported by linear momentum (Poynting's theorem [54]), which is itself conserved and is transported by Maxwell's stresses [2]. We pursue this analogy in §3.3.7.

The cycle-averaged helicity array $\overline{N^{\alpha\beta\gamma}}$ normalised by the energy density

$$w = \frac{1}{2} (\mathbf{E} \cdot \mathbf{E} + \mathbf{B} \cdot \mathbf{B}) \quad (3.47)$$

is

$$\frac{\overline{N^{\alpha\beta\gamma}}}{w} = \pm \frac{\hbar}{\hbar\omega} \hat{k}^\alpha \hat{k}^\beta \hat{k}^\gamma \quad (3.48)$$

for a single circularly polarised plane wave of wave four vector $k^\alpha = (\omega, \mathbf{k})$ and polarisation parameter $\sigma = \pm 1$. The classical result seen in (3.48) reflects the quantum-mechanical results seen in (3.32), (3.7) and (3.36), as we might expect.

3.3.6 On the conservation of helicity, spin and the *ab* infra zilches

The conservation of helicity, the conservation of spin and the conservation of the *ab* infra zilches are seen to constrain the evolution of light in subtly different ways.

To illustrate this, let us consider first a single circularly polarised plane wave of wavevector \mathbf{k} and polarisation parameter $\sigma = \pm 1$, as depicted in figure 3.1(a). Trivially, σ must remain constant in t so as to respect helicity conservation. Suppose, however, that we were to ‘close our eyes’ at $t = t_1$ and open them later, at $t = t_2$, to find that the sign of the wavevector of the wave had changed, as depicted in figure 3.1(b). This hypothetical evolution is clearly unnatural and yet is *not* forbidden by helicity conservation, as

$$\mathcal{H}(t_2) = \mathcal{H}(t_1). \quad (3.49)$$

It *is* forbidden, however, by spin conservation, because

$$\mathcal{S}(t_2) = -\mathcal{S}(t_1) \quad (3.50)$$

which violates the global conservation law seen in (3.16) as $\mathcal{S}(t_1)$ is nonzero.

Consider now the situation depicted in figure 3.2(a). Here we have two circularly polarised plane waves 1 and 2 with equal amplitudes and equal frequencies, propagating in perpendicular directions with wavevectors \mathbf{k}_1 and \mathbf{k}_2 and possessing opposite polarisation parameters $\sigma_1 = \pm 1$ and $\sigma_2 = -\sigma_1$. Suppose we were to ‘close our eyes’ at $t = t_1$ and open them later, at $t = t_2$, to find that both waves had changed the signs of their wavevectors *and* the signs of their polarisation parameters, as depicted in figure 3.2(b). This hypothetical evolution is clearly unnatural and yet is not forbidden by either helicity *or* spin conservation, as

$$\mathcal{H}(t_2) = \mathcal{H}(t_1) = 0 \text{ and } \mathcal{S}(t_2) = \mathcal{S}(t_1). \quad (3.51)$$

It *is* forbidden, however, by the conservation of the *ab* infra zilches, because

$$\mathcal{N}_{(ab)}(t_2) = -\mathcal{N}_{(ab)}(t_1), \quad (3.52)$$

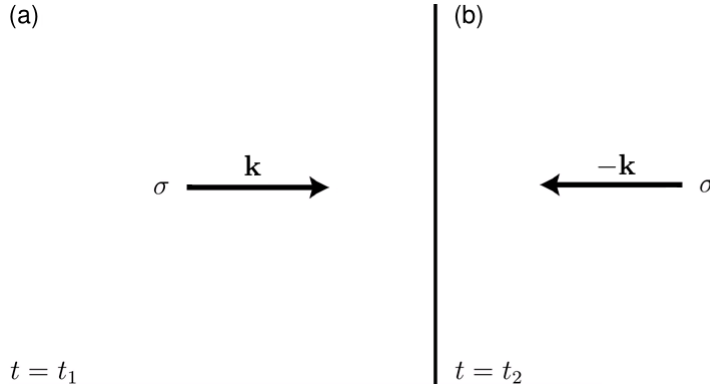


Figure 3.1: (a) A single circularly polarised plane wave of wavevector \mathbf{k} and polarisation parameter σ . (b) The configuration obtained by reversing the sign of the wavevector of the wave.

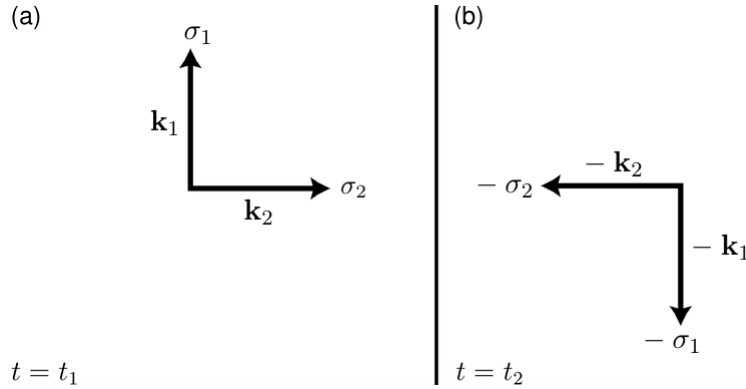


Figure 3.2: (a) A configuration of two circularly polarised plane waves 1 and 2 of equal amplitudes and equal frequencies but with perpendicular wavevectors \mathbf{k}_1 and \mathbf{k}_2 and opposite polarisation parameters σ_1 and $\sigma_2 = -\sigma_1$. (b) The configuration obtained by changing the signs of the wavevectors and polarisation parameters of both waves.

which violates the global conservation law seen in (3.37) as some or all of the $\mathcal{N}_{(ab)}(t_1)$ are non-zero, depending on the coordinate system used. Evidently, helicity conservation, spin conservation and *ab* infra zilch conservation are seen to constrain the evolution of light in subtly different ways, as claimed⁵.

3.3.7 An interesting analogy

The $N^{\alpha\beta 0}$ components of $N^{\alpha\beta\gamma}$ are remarkably similar in form to the contravariant components $T^{\alpha\beta}$ of the energy-momentum tensor⁶, given by [2, 14]

$$T^{\alpha\beta} = \frac{1}{2} \left(F^\alpha_\gamma F^{\gamma\beta} + G^\alpha_\gamma G^{\gamma\beta} \right). \quad (3.53)$$

⁵It is interesting to note, as was pointed out to me by Dr Sonja Franke-Arnold during my viva examination, that the hypothetical transformations depicted in figures 3.1 and 3.2 can be invoked through the use of appropriately orientated plane mirrors during the period in which we have our ‘eyes closed’, although this requires the introduction of charge, of course, in which case helicity, spin, the *ab* infra zilches etc are no longer conserved in general.

⁶It would be fairer, perhaps, to compare $N^{\alpha\beta 0}$ with the contravariant components of the *canonical* energy-momentum tensor: see the discussions in §4.

Explicitly;

$$\begin{aligned} T^{00} &= w, \\ T^{0a} &= g_{(a)}, \\ T^{ab} &= \frac{1}{2}\delta_{(ab)} (\mathbf{E} \cdot \mathbf{E} + \mathbf{B} \cdot \mathbf{B}) - E_{(a)}E_{(b)} - B_{(a)}B_{(b)}. \end{aligned} \quad (3.54)$$

The continuity equation

$$\partial_\beta T^{\alpha\beta} = 0 \quad (3.55)$$

embodies the conservation of energy for $\alpha = 0$ and the conservation of the x , y and z components of linear momentum for $\alpha = 1, 2$ and 3 [2, 14].

We observe that the density components of our helicity array are mapped onto the components of the energy-momentum tensor ($N^{\alpha\beta 0} \rightarrow T^{\alpha\beta}$) when we make the superficial transformation

$$\begin{aligned} \mathbf{A}^\perp &\rightarrow \mathbf{B} \\ \mathbf{C}^\perp &\rightarrow -\mathbf{E} \\ \mathbf{E} &\rightarrow \mathbf{E} \\ \mathbf{B} &\rightarrow \mathbf{B}. \end{aligned} \quad (3.56)$$

An explanation of this follows from the fact that

$$\mathbf{A}^\perp = \pm \frac{\hbar}{\hbar\omega} \mathbf{B}, \quad (3.57)$$

$$\mathbf{C}^\perp = \mp \frac{\hbar}{\hbar\omega} \mathbf{E} \quad (3.58)$$

for a single circularly polarised plane wave of angular frequency ω and polarisation parameter $\sigma = \pm 1$. Any freely propagating light can be regarded as a superposition of circularly polarised plane waves. From (3.58) we have then that the transformation seen in (3.56) is equivalent to letting $\pm\hbar \rightarrow \hbar\omega$ for each of these waves, which is simply a mapping of photon helicity to photon energy. Thus, $N^{\alpha\beta 0} \rightarrow T^{\alpha\beta}$.

Evidently, helicity is much to spin what energy is to linear momentum⁷.

3.3.8 Some explicit calculations

It is difficult, perhaps, to fully appreciate the characteristics of, and indeed the distinctions between, helicity, spin and the ab zilches when considering light that is comprised of a single plane wave. These become more apparent, however, when considering light that is comprised of two or more

⁷Such analogies can be extended to the infinite collection of intrinsic rotation angular momenta discussed in §3.3.4: we observe the existence of an infinite collection of conserved properties of light that depend upon photon energy, the r th $r \in \{0, 1, \dots\}$ member of which takes on a value of $\hbar\omega \hat{k}_{(a)} \hat{k}_{(b)} \hat{k}_{(c)} \dots$ per plane-wave-mode photon of wavevector \mathbf{k} , with r components of $\hat{\mathbf{k}}$ present here. These quantities are manifestly independent of t . For $r = 0$, we have \mathcal{W} and for $r = 1$ we have the components $\mathcal{G}_{(a)}$ of linear momentum \mathcal{G} .

plane waves, as we now demonstrate in three examples.

Example one: interference and quasi-interference

First, we explore further the analogy between energy and helicity which we introduced in §3.3.5 and §3.3.7.

In general, the energy density w is positive, although it can vanish at certain points in space at certain times. In contrast, the helicity density h can be positive, vanishing or *negative*. w is sensitive to the phenomenon of *interference*, as manifest in the presence of the dot products $\mathbf{E} \cdot \mathbf{E}$ and $\mathbf{B} \cdot \mathbf{B}$: interference is maximised when parallel electric fields and / or parallel magnetic flux densities are superposed but is absent in the orthogonal case. In contrast, h is not inherently sensitive to interference but rather, we suggest by analogy, to a kind of ‘interference’ between the electric field \mathbf{E} and magnetic flux density \mathbf{B} and the associated second \mathbf{C}^\perp and first \mathbf{A}^\perp potentials, as manifest in the presence of the dot products $-\mathbf{C}^\perp \cdot \mathbf{E}$ and $\mathbf{A}^\perp \cdot \mathbf{B}$. We refer to this phenomenon as *quasi-interference*.

Let us illustrate these ideas by considering light comprised of a superposition of two linearly polarised plane waves 1 and 2 of equal angular frequency ω . Initially, we suppose that the wavevectors of the waves are equal. Now, let the polarisations of the waves be parallel. The electric fields and the magnetic flux densities of the waves are also parallel and the waves therefore interfere. The electric field and magnetic flux density of each wave are orthogonal, however, to the associated potentials of the other wave and the waves therefore do not exhibit quasi-interference. The nature of the interference (constructive or destructive) is dictated by the relative phase of the waves which influences the amplitude of the (linearly polarised) light. w can be greater than, equal to or less than the sum of the energy densities attributable to the waves individually whereas h vanishes. If we suppose instead that the polarisations of the waves are orthogonal, the electric fields and the magnetic flux densities of the waves are also orthogonal and the waves therefore do not interfere. The electric field and magnetic flux density of each wave are parallel, however, to the associated potentials of the other wave and the waves therefore exhibit quasi-interference. The nature of the quasi-interference is also dictated by the relative phase of the waves which now influences the polarisation of the (elliptically polarised in general) light. w is simply the sum of the energy densities attributable to the waves individually whereas h assumes a value equivalent to $\sigma\hbar$ ‘per photon’. If the light is of left-handed circular polarisation ($\sigma = +1$), \mathbf{A}^\perp and \mathbf{C}^\perp are in phase with, and are parallel and anti-parallel respectively to, \mathbf{B} and \mathbf{E} respectively, giving rise to a positive h . Opposing relative orientations are found if the light is of right-handed circular polarisation ($\sigma = -1$), giving rise to a negative h . If the light is linearly polarised ($\sigma = 0$), however, \mathbf{A}^\perp and \mathbf{C}^\perp are a quarter cycle out of phase with, and are orthogonal to, \mathbf{B} and \mathbf{E} respectively, giving rise to a vanishing h . These facts are depicted in figure 3.3. Zambrini and Barnett have made observations that are closely related to those made here [79].

Let us now consider what happens when the wavevectors \mathbf{k}_1 and \mathbf{k}_2 of the waves lie within the x - z plane but make angles of $\pm\theta$ ($\theta > 0$) with the $+z$ axis, thus being separated by an angle of 2θ . We take the amplitudes E_0 of the waves to be equal and suppose that the polarisation of wave

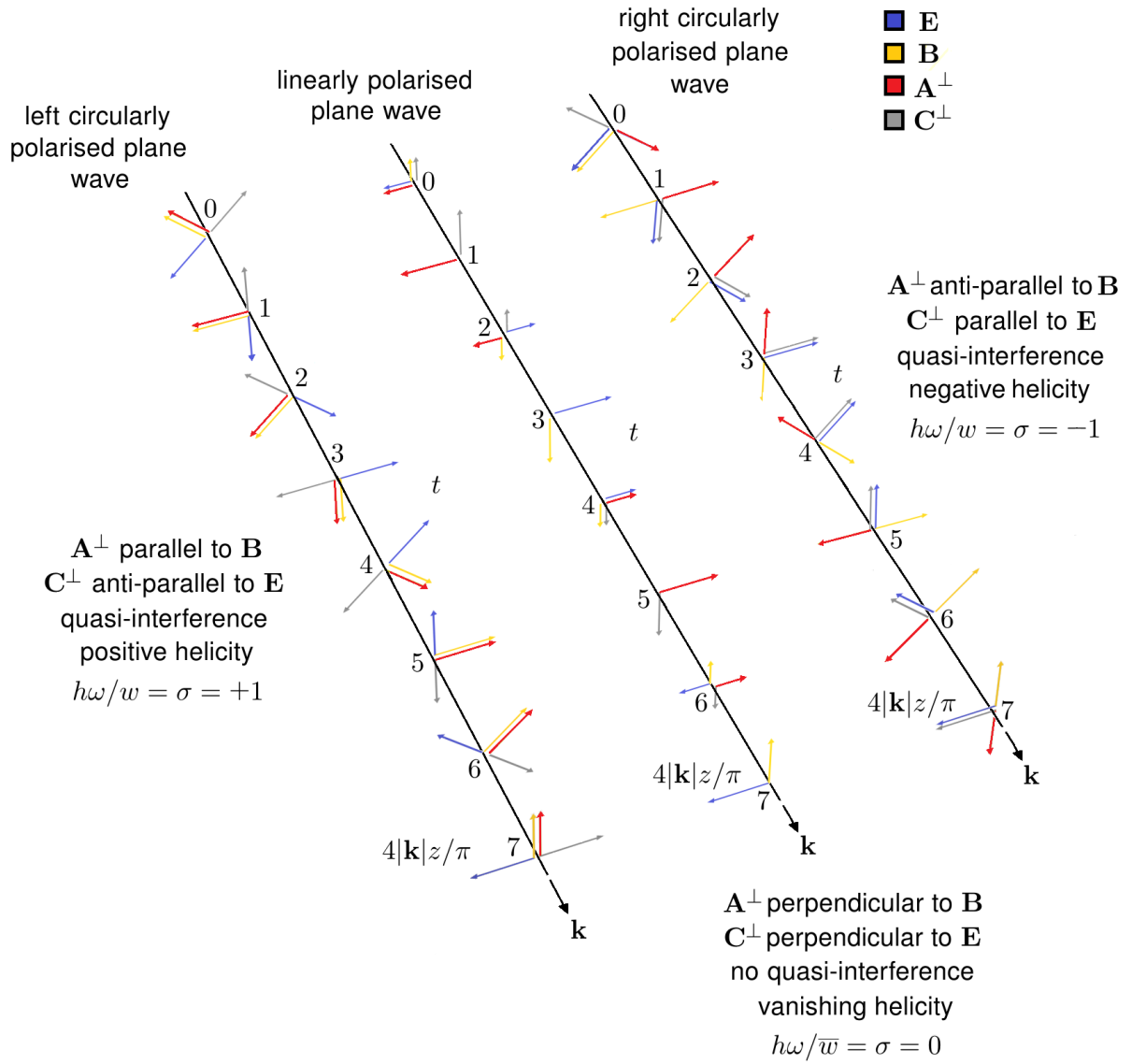


Figure 3.3: Three plane waves of wavevector \mathbf{k} , angular frequency $\omega = |\mathbf{k}|$ and differing polarisations. For each wave, the value taken by the helicity density h , which is sensitive to quasi-interference, should be compared with the relative orientations and phases of \mathbf{A}^\perp and \mathbf{B} as well as \mathbf{C}^\perp and \mathbf{E} .

1 is confined to the x - z plane whilst the polarisation of wave 2 makes an angle ϑ with this plane. Explicitly, we describe the light as seen in (1.75)-(1.80) with the complex quantites $\tilde{\mathbf{E}}$ and $\tilde{\mathbf{B}}$ given here by

$$\begin{aligned} \tilde{\mathbf{E}} = & E_0(\hat{\mathbf{x}} \cos \theta - \hat{\mathbf{z}} \sin \theta) \exp[i|\mathbf{k}|(z \cos \theta + x \sin \theta)] \\ & + E_0[(\hat{\mathbf{x}} \cos \theta + \hat{\mathbf{z}} \sin \theta) \cos \vartheta + \hat{\mathbf{y}} \sin \vartheta] \exp[i|\mathbf{k}|(z \cos \theta - x \sin \theta)], \end{aligned} \quad (3.59)$$

$$\begin{aligned} \tilde{\mathbf{B}} = & E_0 \hat{\mathbf{y}} \exp[i|\mathbf{k}|(z \cos \theta + x \sin \theta)] \\ & + E_0[(-\hat{\mathbf{x}} \cos \theta - \hat{\mathbf{z}} \sin \theta) \sin \vartheta + \hat{\mathbf{y}} \cos \vartheta] \exp[i|\mathbf{k}|(z \cos \theta - x \sin \theta)]. \end{aligned} \quad (3.60)$$

We find that

$$\bar{w} = E_0^2 [1 + \cos \vartheta \cos (\kappa x)], \quad (3.61)$$

$$h = -E_0^2 \sin \vartheta \sin (\kappa x) / \omega, \quad (3.62)$$

to first order in θ , with $\kappa = 2\theta\omega$ a wavenumber. Notice that h is independent of t , as is the case for all strictly monochromatic light that is freely propagating. Due to the small angular separation 2θ of the waves, their relative phase undulates as a function of x , with wavelength $2\pi/\kappa = \pi/\theta\omega$. For $\vartheta = 0$, the polarisations of the waves are (essentially, as θ is small) parallel and the light is linearly polarised. The waves interfere and \bar{w} undulates between $2E_0$ and 0, reflecting the undulation of the relative phase of the waves. Thus, we have ‘bright’ and ‘dark’ fringes: a redistribution of energy within the light, attributable to constructive interference and destructive interference. In contrast, no quasi-interference occurs and h vanishes. Light possessing such characteristics can be found, for example, in the far-field of a Young’s double slit diffraction pattern using linearly polarised light [36]. If, instead, $\vartheta = \pi/2$, the polarisations of the waves are orthogonal and the polarisation parameter σ of the light undulates between $\sigma = 1$ and $\sigma = -1$, again reflecting the undulation of the relative phase of the waves. The waves do not interfere and \bar{w} assumes a value of E_0^2 . The waves do, however, exhibit quasi-interference and h undulates between E_0^2/ω and $-E_0^2/\omega$. Thus, we have ‘helicity fringes’: a redistribution of helicity about $h = 0$ within the light, attributable to quasi-interference. Such light has been utilised recently in optical trapping experiments [80, 81] and has been referred to as a polarisation grating. See also [82].

Example two: helicity is analogous to charge

Although we are considering light that is propagating freely in the strict absence of charge, we can draw an analogy between the helicity continuity equation (3.44) and the charge continuity equation (1.35). In doing so, we elucidate the distinction between helicity and spin.

Charge, and indeed the charge density ρ can be positive or negative and a flow of positive charge in a given direction can yield the same current density \mathbf{J} as a suitable flow of negative charge in the opposite direction [36]. Similarly, helicity, and indeed the helicity density h can be positive or negative and a flow of positive helicity in a given direction can yield the same helicity flux density \mathbf{s} as a suitable flow of negative helicity in the opposite direction. The analogy stops there, however, as there is no obvious physical significance to the volume integral of \mathbf{J} whereas \mathbf{s} is also a spin density, the volume integral of which over all space yields the spin \mathcal{S} , of course.

To illustrate these ideas, let us consider light comprised of two circularly polarised plane waves 1 and 2 of equal amplitude $E_0/\sqrt{2}$, and equal angular frequency ω propagating in the $+z$ and $-z$ directions and possessing polarisation parameters $\sigma_1, \sigma_2 \in \{-1, 1\}$. Explicitly, we describe the light as seen in (1.75)-(1.80) with the complex quantites $\tilde{\mathbf{E}}$ and $\tilde{\mathbf{B}}$ given here by

$$\tilde{\mathbf{E}} = E_0(\hat{\mathbf{x}} + i\sigma_1\hat{\mathbf{y}}) \exp(i|\mathbf{k}|z)/\sqrt{2} + E_0(-\hat{\mathbf{x}} + i\sigma_2\hat{\mathbf{y}}) \exp(-i|\mathbf{k}|z)/\sqrt{2}, \quad (3.63)$$

$$\tilde{\mathbf{B}} = E_0(-i\sigma_1\hat{\mathbf{x}} + \hat{\mathbf{y}}) \exp(i|\mathbf{k}|z)/\sqrt{2} + E_0(i\sigma_2\hat{\mathbf{x}} + \hat{\mathbf{y}}) \exp(-i|\mathbf{k}|z)/\sqrt{2}. \quad (3.64)$$

We find that

$$h = E_0^2 (\sigma_1 + \sigma_2) / 2\omega, \quad (3.65)$$

$$\mathbf{s} = E_0^2 (\sigma_1 - \sigma_2) \hat{\mathbf{z}} / 2\omega. \quad (3.66)$$

Notice that \mathbf{s} , like h , is independent of t , as is the case for all strictly monochromatic light that is freely propagating.

If both waves possess the *same* sense of circular polarisation ($\sigma_1 = \sigma_2 = \pm 1$), there is a non-vanishing helicity density $h = \pm E_0^2 / \omega$ but a vanishing helicity flux density or spin density $\mathbf{s} = 0$. In contrast, if the waves possess *opposite* circular polarisations ($\sigma_1 = -\sigma_2 = \pm 1$), there is a vanishing helicity density $h = 0$ but a non-vanishing helicity flux density or spin density $\mathbf{s} = \pm E_0 \hat{\mathbf{z}} / \omega$. Returning to the analogy made above between helicity and charge, we can liken the first case ($\sigma_1 = \sigma_2 = \pm 1$) to a combination of two counterpropagating flows of charge of the *same* sign, giving rise to a net charge (cf $h \neq 0$) but no net current (cf $\mathbf{s} = 0$). In contrast, we can liken the second case ($\sigma_1 = -\sigma_2 = \pm 1$) to a combination of two counterpropagating flows of charge of *opposite* sign, yielding overall neutrality (cf $h = 0$) whilst giving rise to a net current (cf $\mathbf{s} \neq 0$). See figure 3.4. Counterpropagating circularly polarised beams of light possessing *opposite* handedness (but slightly different amplitudes) have been utilised recently in a luminescence-detected circular dichroism experiment [83–85], which yielded an enhancement of a certain measure of dissymmetry over that which can be observed utilising a single traveling beam of circularly polarised light. Counterpropagating circularly polarised beams of light possessing the *same* handedness comprise so-called $\sigma - \sigma$ light which is utilised in the laser cooling of atoms [86–90].

Evidently, it is possible to produce light that possesses a non-vanishing helicity but a vanishing helicity flux and, in particular, a vanishing spin (and vice-versa). This is, we suggest, a clear demonstration that helicity and spin are indeed distinct, in spite of the intimate relationship between them which is embodied in the helicity continuity equation (3.44).

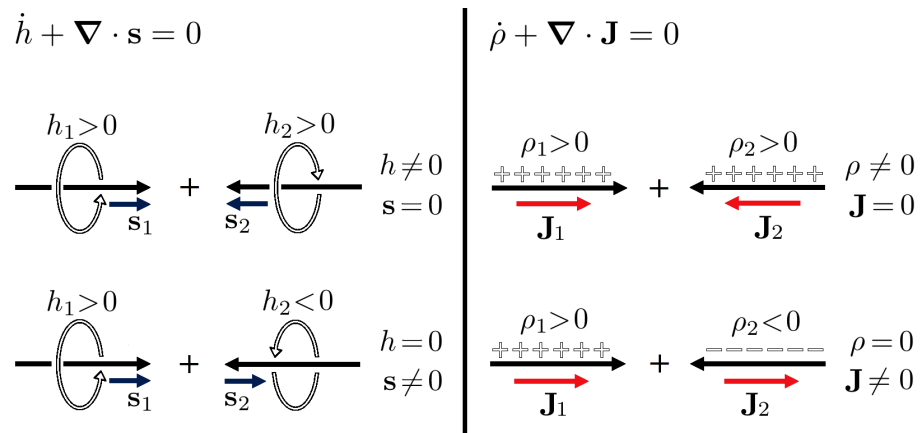


Figure 3.4: A close analogy can be drawn between helicity and charge owing primarily to the fact that both are *signed* quantities.

Example three: helicity and polarisation are not synonymous

Let us now highlight the distinction between helicity and polarisation. Helicity is an intrinsic rotation angular momentum and may be thought of as flowing continuously within an optical field, in accordance with the helicity continuity equation (3.44). In contrast, polarisation is a concept which is invoked to describe the manner in which the *electric* field vectors, in particular, evolve. For a single circularly polarised plane wave, the helicity is certainly seen to *depend* upon the polarisation and, for this reason, the words ‘helicity’ and ‘polarisation’ are often used interchangeably. It should be clear, however, that they are not synonymous in general. To illustrate this, we need only note that horizontal and linear polarisations are distinct from each other and yet both give rise to the same (vanishing) helicity. To quote Darwin: “the polarisation of ... light is incompletely described by ... angular momentum” [24].

We can demonstrate that the direct identification of helicity with rotating electric field vectors (circular polarisation) is not appropriate in general through an examination of light comprised of two plane waves 1 and 2 of equal amplitude E_0 and equal angular frequency ω that are linearly polarised parallel to the y and x axes and propagate in the $+z$ and $-z$ directions. Explicitly, we describe the light as seen in (1.75)-(1.80) with the complex quantites $\tilde{\mathbf{E}}$ and $\tilde{\mathbf{B}}$ given here by

$$\tilde{\mathbf{E}} = E_0 \hat{\mathbf{y}} \exp(i|\mathbf{k}|z) - E_0 \hat{\mathbf{x}} \exp(-i|\mathbf{k}|z), \quad (3.67)$$

$$\tilde{\mathbf{B}} = -E_0 \hat{\mathbf{x}} \exp(i|\mathbf{k}|z) - E_0 \hat{\mathbf{y}} \exp(-i|\mathbf{k}|z). \quad (3.68)$$

This is so-called lin \perp lin light which is utilised, for example, in the laser cooling of atoms, due to its inherent ‘polarisation gradients’ [86–90]: at $z = z_N = N\pi/2\omega$ and $z = z_M = (2M+1)\pi/4\omega$ with $N, M \in \{0, \pm 1, \dots\}$, the electric field vectors oscillate within the x - y plane in linear and circular manners, respectively. The magnetic flux density pseudovectors also oscillate within the x - y plane in linear and circular manners at $z = z_N$ and $z = z_M$, respectively. However, the sense of rotational motion that they exhibit is *opposite* to that exhibited by the electric field vectors. We find that

$$h = 0, \quad (3.69)$$

$$s = 0, \quad (3.70)$$

which is unsurprising, perhaps, given these opposing rotational motions: h and s favour neither the electric nor magnetic properties of light. Evidently, the mere existence of rotating electric field vectors (circular polarisation) does not in itself imply the existence of a non-vanishing h and / or s , in general⁸.

⁸Although \mathbf{E} and \mathbf{B} are treated in an equal manner by Maxwell’s equations as written in the strict absence of charge (1.68)-(1.71), they are, of course, distinct entities. In spite of the opposing senses of rotational motion exhibited by their vectors and pseudovectors, it would certainly *not* be fair to say that the light under examination possesses no rotational motion whatsoever. \mathbf{E} and \mathbf{B} do not ‘cancel each other out’. Indeed, further investigation reveals the presence of non-vanishing spin flux density components or *ab* infra zilches densities $n_{(ab)}$.

3.4 The zilch

In 1964, Lipkin [78] introduced a rank-three pseudotensor $Z^{\alpha\beta\gamma}$ with contravariant components expressible as

$$\begin{aligned} Z^{000} &= \frac{1}{2} [\mathbf{E} \cdot (\nabla \times \mathbf{E}) + \mathbf{B} \cdot (\nabla \times \mathbf{B})], \\ Z^{0a0} &= \frac{1}{2} (\mathbf{E} \times \dot{\mathbf{E}} + \mathbf{B} \times \dot{\mathbf{B}})_{(a)}, \\ Z^{ab0} &= \frac{1}{2} \left\{ \delta_{(ab)} [\mathbf{E} \cdot (\nabla \times \mathbf{E}) + \mathbf{B} \cdot (\nabla \times \mathbf{B})] \right. \\ &\quad \left. - E_{(a)} (\nabla \times \mathbf{E})_{(b)} - E_{(b)} (\nabla \times \mathbf{E})_{(a)} - B_{(a)} (\nabla \times \mathbf{B})_{(b)} - B_{(b)} (\nabla \times \mathbf{B})_{(a)} \right\} \end{aligned} \quad (3.71)$$

and

$$\begin{aligned} Z^{00a} &= Z^{0a0}, \\ Z^{0ab} &= Z^{ab0}, \\ Z^{abc} &= \delta_{(ab)} Z^{00c} + \frac{1}{2} [-E_{(a)} \partial_c B_{(b)} - E_{(b)} \partial_c B_{(a)} + B_{(a)} \partial_c E_{(b)} + B_{(b)} \partial_c E_{(a)}], \end{aligned} \quad (3.72)$$

where we have introduced a factor of 1/2 and omitted solenoidal contributions to the $Z^{\alpha\beta\alpha}$. The significance of $Z^{\alpha\beta\gamma}$ lies in the fact that it obeys the continuity equation

$$\partial_\gamma Z^{\alpha\beta\gamma} = 0 \quad (3.73)$$

which embodies the conservation of the quantities

$$\mathcal{Z}^{\alpha\beta} = \iiint Z^{\alpha\beta 0} d^3\mathbf{r}. \quad (3.74)$$

Lipkin referred to these collectively as the zilch, with $\mathcal{Z}^{\alpha\beta}$ in particular the $\alpha\beta$ zilch. By virtue of the symmetry $\mathcal{Z}^{\alpha\beta} = \mathcal{Z}^{\beta\alpha}$ and the fact that $\mathcal{Z}^\alpha_\alpha = 0$, nine of the $\mathcal{Z}^{\alpha\beta}$ are distinct.

Following Lipkin, we find that

$$\frac{\overline{Z^{\alpha\beta\gamma}}}{w} = \pm \frac{\hbar\omega^2}{\hbar\omega} \hat{k}^\alpha \hat{k}^\beta \hat{k}^\gamma \quad (3.75)$$

for a circularly polarised plane wave of wave four vector $k^\alpha = (\omega, \mathbf{k})$ and polarisation parameter $\sigma = \pm 1$, which suggests an $\alpha\beta$ zilch of $\pm \hbar\omega^2 \hat{k}^\alpha \hat{k}^\beta$ per photon as is indeed the case. Evidently then, the cycle-averaged components $\overline{Z^{\alpha\beta\gamma}}$ of $Z^{\alpha\beta\gamma}$ are, for this wave, proportional to the cycle-averaged components $\overline{N^{\alpha\beta\gamma}}$ of $N^{\alpha\beta\gamma}$, as may be seen by comparing (3.75) with (3.48). It can be shown, in fact, that

$$\overline{Z^{\alpha\beta\gamma}} = \omega^2 \overline{N^{\alpha\beta\gamma}} \quad (3.76)$$

for *any* monochromatic light of angular frequency ω . This suggests, perhaps, that the zilch might provide a description of the intrinsic rotation angular momentum of light that is similar to that presented in §3.3 whilst avoiding the explicit appearance of non-local functions of the electric field \mathbf{E} and the magnetic flux density \mathbf{B} , such as the first potential \mathbf{A}^\perp and the second potential \mathbf{C}^\perp . Indeed, Lipkin

himself noted that the zilch might be related to the ‘intrinsic spin’ of light, although he acknowledged the unusual frequency dependence exhibited by the zilch and observed that the dimensions of the zilch cannot readily be brought into coincidence with those of an angular momentum. Shortly after the appearance of Lipkin’s paper, it was conjectured by Candlin [69] that the zilch is but one member of an infinite hierarchy of conserved properties of light related to but distinct from helicity and that they possess no obvious physical significance. Generalisations of Lipkin’s discovery were also made by Morgan [91], O’Connell and Tompkins [92] and Kibble [93]. Nevertheless, the zilch was recently reintroduced into the literature by Tang, Cohen and Yang [83, 94] who referred to Z^{000} in particular as the ‘optical chirality’, advocating it as a measure of the chirality of light. This interpretation has been utilised to predict and describe the results of luminescence-detected circular dichroism experiments [83–85, 94–96]. Restricting their attention to monochromatic light, of angular frequency ω , Bliokh and Nori [97] recognised, much in the spirit of Lipkin’s original observations, that Z^{00} and the Z^{0a} are, in a given frame of reference, proportional to, but *not* equal to, the helicity \mathcal{H} and the components $S_{(a)}$ of the spin \mathcal{S} , the proportionality factor being ω^2 . Such proportionalities were also observed by Andrews and Coles [98–100].

To be clear, it is the helicity, spin, *ab* infra zilches etc that possess the dimensions of a rotation angular momentum and describe the angular momentum of light. The zilch, in contrast, lacks the dimensions that are required in this context and does not describe the angular momentum of light. We explain the significance of the zilch, in particular the apparent similarity of the 00 zilch to helicity, the 0a zilches to the components of spin and the *ab* zilches to the *ab* infra zilches, by recalling from §2.2 that the time derivatives or curls \mathbf{G} and \mathbf{M} of \mathbf{E} and \mathbf{B} also satisfy a set of Maxwell-like equations (2.18)-(2.21). It follows that the superficial transformation

$$\begin{aligned}\mathbf{A}^\perp &\rightarrow \dot{\mathbf{A}}^\perp = \nabla \times \mathbf{C}^\perp \\ \mathbf{C}^\perp &\rightarrow \dot{\mathbf{C}}^\perp = -\nabla \times \mathbf{A}^\perp \\ \mathbf{E} &\rightarrow \dot{\mathbf{E}} = \nabla \times \mathbf{B} \\ \mathbf{B} &\rightarrow \dot{\mathbf{B}} = -\nabla \times \mathbf{E}\end{aligned}\tag{3.77}$$

applied to $N^{\alpha\beta\gamma}$ yields another set of conserved quantities which describe the ‘angular momentum’ of the time derivative or curl (\mathbf{G} and \mathbf{M}) of the electromagnetic field, rather than the electromagnetic field (\mathbf{E} and \mathbf{B}) itself. These quantities are, in fact, the zilch: the transformation seen in (3.77) takes $N^{\alpha\beta\gamma} \rightarrow Z^{\alpha\beta\gamma}$. Thus, the 00 zilch is the ‘helicity’ of the time derivative or curl of the electromagnetic field, the 0a zilches are the components of the ‘spin’ of the time derivative or curl of the electromagnetic field and the *ab* zilches are the ‘*ab* infra zilches’ of the time derivative or curl of the electromagnetic field, hence our choice of name for the latter. Indeed, we recognise now that

$$Z^{00} = \iiint \frac{1}{2} (\dot{\mathbf{A}}^\perp \cdot \dot{\mathbf{B}} - \dot{\mathbf{C}}^\perp \cdot \dot{\mathbf{E}}) d^3\mathbf{r},\tag{3.78}$$

for example, which should be compared with the form for \mathcal{H} seen on the first line of (3.31). The appearance of two time derivatives in (3.78) and analogously for the other $Z^{\alpha\beta}$ gives rise in turn to the proportionality seen in (3.76). That the Lorentz transformation properties of Z^{00} differ from those

of \mathcal{H} is seemingly a reflection of the fact that the Lorentz transformation properties of \mathbf{G} and \mathbf{M} differ from those of \mathbf{E} and \mathbf{B} . Indeed, the Maxwell-like equations (2.18)-(2.21) are

$$\begin{aligned}\partial_\beta \partial_0 F^{\alpha\beta} &= 0, \\ \partial_\beta \partial_0 G^{\alpha\beta} &= 0,\end{aligned}\tag{3.79}$$

and may be seen to follow from the general observation that all contractions of the tensor $\partial_\alpha \partial_\beta \dots \partial_\omega F^{\mu\nu}$ and the pseudotensor $\partial_\alpha \partial_\beta \dots \partial_\omega G^{\mu\nu}$ vanish.

3.5 Extrinsic and quasi-extrinsic rotation angular momenta

In §3.3, we considered intrinsic rotation angular momenta. That is, helicity, spin, the *ab* infra zilches etc. In the present section, we turn our attention to extrinsic and quasi-intrinsic rotation angular momenta. That is, orbital angular momentum and possible extensions thereof.

3.5.1 Orbital angular momentum

Here, we introduce a *local* description of orbital angular momentum. Adopting the orbital angular momentum density \mathbf{l} seen in (3.12) and identifying the components

$$o_{(ab)} = \frac{1}{2} \left\{ \epsilon_{(acd)} \epsilon_{(bef)} \left[E_{(e)} r_{(c)} \partial_d C_{(f)}^\perp - B_{(e)} r_{(c)} \partial_d A_{(f)}^\perp \right] + A_{(a)}^\perp B_{(b)} - C_{(a)}^\perp E_{(b)} \right\} \tag{3.80}$$

of an associated orbital angular momentum flux density, we obtain the continuity equation

$$\dot{l}_{(a)} + \partial_b o_{(ab)} = 0 \tag{3.81}$$

which embodies the conservation of orbital angular momentum. Whilst writing this thesis, the orbital angular momentum continuity equation (3.81) was also identified, independently, by Bliokh, Dressel and Nori [101].

For the Bessel beam described by (1.81)-(1.84),

$$\frac{\bar{l}_z}{\bar{w}} = \frac{\hbar \ell}{\hbar \omega}. \tag{3.82}$$

This classical result (3.82) suggests a z component of orbital angular momentum equal to $\hbar \ell$ per photon, as we might expect.

3.5.2 Orbital helicity?

In light of our observation in §3.3 that spin is but one member of an infinite collection of intrinsic rotation angular momenta (helicity, spin, the *ab* infra zilches etc) it is natural, perhaps, to ask whether orbital angular momentum is also but one member of an analogous collection. It appears that this is *not* the case, however. In particular, we are unable to identify a non-vanishing orbital analogue of helicity.

In particle physics, the fact is well established that the orbital angular momentum of a particle makes no contribution to the particle's helicity, as

$$(\hat{\mathbf{r}} \times \hat{\mathbf{p}}) \cdot \frac{\hat{\mathbf{p}}}{|\hat{\mathbf{p}}|} = 0. \quad (3.83)$$

This relationship has been emphasised in the context of light by Fernandez-Corbaton, Zambrana-Puyalto and Molina-Terizza [102]. Looking at the second line of (3.8), we see indeed that the orbital angular momentum density in reciprocal space is everywhere orthogonal to the wavevector \mathbf{k} and so the component of this density along \mathbf{k} vanishes. Another indication follows from the observation that the trace of the components of the spin flux density $n_{(ab)}$ yields the helicity density h ($n_{(aa)} = h$): pursuing an analogous approach for orbital angular momentum, we find that

$$\iiint_{\infty} o_{(aa)} d^3\mathbf{r} = 0, \quad (3.84)$$

again suggesting the absence of a non-trivial orbital analogue of helicity.

It may be surprising that the intrinsic rotation angular momentum content of light is so rich, being comprised of helicity, spin, the *ab* infra zilches etc, whilst the extrinsic and quasi-extrinsic rotation angular momentum content of light is relatively barren, being comprised solely of orbital angular momentum. Here, it is instructive, perhaps, to note that these have rather different 'origins': the former (helicity, spin, the *ab* infra zilches etc) as conserved quantities are *specific* to light, owing their existence in particular to the spin-one and massless nature of the photon. In contrast, the latter (orbital angular momentum) is *not* specific to light, being a rather general property of waves: electron de Broglie waves [103] and sound waves [51] are but two examples in which orbital angular momentum can manifest owing to the presence of helical phase fronts.

3.6 Boost angular momenta

In §3.3-§3.5 we considered *rotation* angular momenta. We now turn our attention towards the other side of the story; *boost* angular momenta.

3.6.1 Intrinsic boost angular momenta

Following Barnett's proposed separation of the boost angular momentum \mathcal{K} into boost spin \mathcal{V} and boost orbital \mathcal{Y} pieces [45], discussed in §3.1, we observe here the existence of an infinite collection of boost analogues of the intrinsic rotation angular momenta (helicity, spin, the *ab* infra zilches etc) introduced in §3.3.

We identify

$$d = -\frac{1}{2} \left(\mathbf{A}^\perp \cdot \mathbf{E} + \mathbf{C}^\perp \cdot \mathbf{B} \right) \quad (3.85)$$

as a boost helicity density: together with a boost helicity flux density

$$\mathbf{v} = \frac{1}{2} \left(-\mathbf{E} \times \mathbf{C}^\perp + \mathbf{B} \times \mathbf{A}^\perp \right), \quad (3.86)$$

it satisfies the continuity equation

$$\dot{d} + \nabla \cdot \mathbf{v} = 0, \quad (3.87)$$

which embodies the conservation of boost helicity and is seemingly analogous to the helicity continuity equation (3.44). We also recognise \mathbf{v} as being the integrand of \mathcal{V} seen in (3.26) and therefore identify it as a boost spin density: together with the components

$$q_{(ab)} = \frac{1}{2} \left[\delta_{(ab)} \left(-\mathbf{A}^\perp \cdot \mathbf{E} + \mathbf{C}^\perp \cdot \mathbf{B} \right) + A_{(a)}^\perp E_{(b)} + A_{(b)}^\perp E_{(a)} + C_{(a)}^\perp B_{(b)} + C_{(b)}^\perp B_{(a)} \right] \quad (3.88)$$

of a boost spin flux density, it satisfies the continuity equation

$$\dot{v}_{(a)} + \partial_b q_{(ab)} = 0, \quad (3.89)$$

which embodies the conservation of boost spin and is seemingly analogous to the spin continuity equation (3.45). We can proceed in this vein indefinitely and thus identify an infinite collection of intrinsic boost angular momenta, as claimed.

The boost helicity density d and the boost helicity flux density or boost spin density \mathbf{v} can certainly be non-vanishing at a given position \mathbf{r} and time t . Their cycle-averaged values \bar{d} and $\bar{\mathbf{v}}$ vanish for all monochromatic light, however, and the boost helicity \mathcal{D} itself vanishes:

$$\begin{aligned} \mathcal{D} &= \iiint_{\infty} d \, d^3\mathbf{r} \\ &= 0 \end{aligned} \quad (3.90)$$

in general, just as \mathcal{V} does ($\mathcal{V} = 0$). The remaining members of the infinite collection of intrinsic boost angular momenta are, it seems, similarly fickle. We offer an explanation for this in §4.4.5.

3.6.2 Extrinsic boost angular momenta

Much as we can identify a continuity equation (3.89) for boost spin, we can identify an explicit continuity equation for boost orbital angular momentum. Taking the integrand

$$\mathbf{y} = \frac{1}{2} \left[-A_{(a)}^\perp \left(t \nabla + \mathbf{r} \frac{\partial}{\partial t} \right) E_{(a)} - C_{(a)}^\perp \left(t \nabla + \mathbf{r} \frac{\partial}{\partial t} \right) B_{(a)} \right] \quad (3.91)$$

of Barnett's candidate \mathfrak{Y} for the boost orbital angular momentum [45], seen in (3.27), to be a boost orbital angular momentum density and introducing the components

$$f_{(ab)} = \frac{1}{2} \left(t \left\{ \delta_{(ab)} \frac{1}{2} \left[\partial_c C_{(d)}^\perp \partial_d C_{(c)}^\perp + \partial_c A_{(d)}^\perp \partial_d A_{(c)}^\perp \right] - A_{(c)}^\perp \partial_a \partial_b A_{(c)}^\perp - C_{(c)}^\perp \partial_a \partial_b C_{(c)}^\perp \right\} \right. \\ \left. + r_{(a)} \left[A_{(c)}^\perp \partial_b E_{(c)} + C_{(c)}^\perp \partial_b B_{(c)} - \partial_c C_{(b)}^\perp B_{(c)} - \partial_c A_{(b)}^\perp E_{(c)} \right] + A_{(a)}^\perp E_{(b)} + C_{(a)}^\perp B_{(b)} \right) \quad (3.92)$$

of an associated boost orbital angular momentum flux density, we identify the continuity equation

$$\dot{y}_{(a)} + \partial_b f_{(ab)} = 0, \quad (3.93)$$

which embodies the conservation of boost orbital angular momentum and is seemingly analogous the orbital angular momentum continuity equation (3.81). Owing to the trivial nature of boost spin, the continuity equation (3.93) does not obviously contain any physical information not already present, however, in the continuity equation

$$\partial_\alpha M^{0a\alpha} = 0, \quad (3.94)$$

from (3.14), which embodies the conservation of the *complete* (spin + orbital) boost angular momentum.

As was observed in §3.5.2, a trace over the spin flux density components $n_{(ab)}$ yields the helicity density h ($n_{(aa)} = h$) whilst a trace over the orbital angular momentum flux density components $o_{(ab)}$ yields a candidate orbital helicity density, the integral over all space of which vanishes, as seen in (3.84). When looking at boost angular momentum rather than rotation angular momentum, the situation is somewhat reversed: a trace over the boost spin flux density components $q_{(ab)}$ yields the boost helicity density d ($q_{(aa)} = d$), the integral over all space of which vanishes, as seen in (3.90). A trace over the boost orbital angular momentum flux density components $f_{(ab)}$, however, yields the density of a non-trivial conserved quantity that we might refer to as boost orbital helicity. For simplicity, we illustrate this for the complete (spin+orbital) form

$$M^{\alpha\beta}{}_\beta = x_\beta T^{\beta\alpha} \\ = D^\alpha \quad (3.95)$$

which satisfies the continuity equation

$$\partial_\alpha D^\alpha = 0 \quad (3.96)$$

embodying the conservation of boost orbital helicity.

We may elucidate the physical significance of boost orbital helicity and its conservation by considering a single linearly polarised plane wave, of angular frequency ω and wavevector \mathbf{k} . Let us identify some point X on the wave that resides at position \mathbf{r}_1 at time t_1 . The boost orbital helicity contained

in an infinitesimal volume element centred upon \mathbf{r}_1 at t_1 is proportional to

$$D^0(\mathbf{r}_1, t_1) = t_1 w(\mathbf{r}_1, t_1) - \mathbf{r}_1 \cdot \mathbf{g}(\mathbf{r}_1, t_1). \quad (3.97)$$

At a time $t_2 > t_1$, the wave has propagated such that the point of interest X resides at a new position \mathbf{r}_2 . The boost orbital helicity contained in an infinitesimal volume element centred upon \mathbf{r}_2 at t_2 is proportional to

$$D^0(\mathbf{r}_2, t_2) = t_2 w(\mathbf{r}_2, t_2) - \mathbf{r}_2 \cdot \mathbf{g}(\mathbf{r}_2, t_2). \quad (3.98)$$

Now, the conservation of energy and linear momentum tells us that

$$w(\mathbf{r}_2, t_2) = w(\mathbf{r}_1, t_1), \quad (3.99)$$

$$\mathbf{g}(\mathbf{r}_2, t_2) = \mathbf{g}(\mathbf{r}_1, t_1). \quad (3.100)$$

Moreover, Poynting's vector \mathbf{g} coincides with the direction of propagation of the wave and so

$$\mathbf{r}_2 = \mathbf{r}_1 + (t_2 - t_1) \hat{\mathbf{g}}(\mathbf{r}_1, t_1). \quad (3.101)$$

Thus

$$D^0(\mathbf{r}_2, t_2) - D^0(\mathbf{r}_1, t_1) = (t_2 - t_1) [w(\mathbf{r}_1, t_1) - |\mathbf{g}(\mathbf{r}_1, t_1)|]. \quad (3.102)$$

The conservation of boost orbital helicity tells us finally that $D^0(\mathbf{r}_2, t_2) - D^0(\mathbf{r}_1, t_1) = 0$. As $t_2 \neq t_1$ and the argument is valid for all \mathbf{r}_1 and t_1 , it follows then from (3.102) that the energy density w and the magnitude of \mathbf{g} are related as

$$w = |\mathbf{g}|. \quad (3.103)$$

Thus, the conservation of boost orbital helicity can be regarded, for a single plane wave at least, as a statement of the dispersion relation $\omega = |\mathbf{k}|$. See figure 3.5.

3.7 In the presence of charge

We now illustrate briefly how the results introduced in the present chapter can be generalised to account for the presence of charge.

We find, for example, that the spin $\mathcal{S} = \mathcal{S}(t)$ and orbital angular momentum $\mathcal{L} = \mathcal{L}(t)$ of the

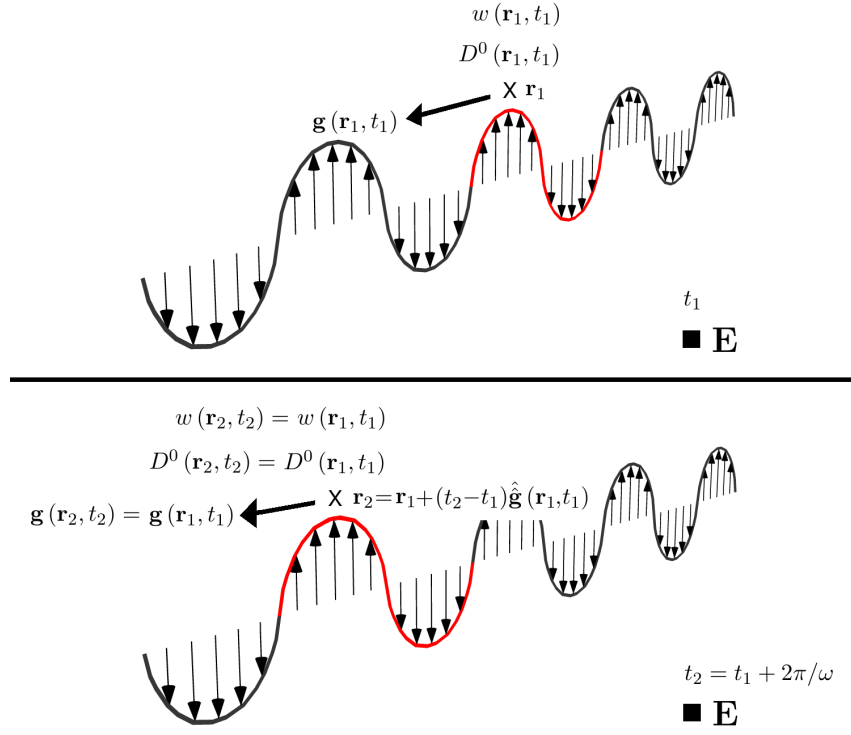


Figure 3.5: The continuity equation $\partial_\alpha D^\alpha = 0$ for boost orbital helicity can be understood or at least appreciated by examining a point X on a single linearly polarised plane wave of angular frequency ω and wavevector \mathbf{k} (for the sake of clarity, a portion of the wave surrounding X is highlighted here in red). Like the energy $w(\mathbf{r}_1, t_1)d^3\mathbf{r}$ and the linear momentum $\mathbf{g}(\mathbf{r}_1, t_1)d^3\mathbf{r}$, the boost orbital helicity $D^0(\mathbf{r}_1, t_1)d^3\mathbf{r}$ contained in the vicinity of X is conserved and is therefore carried along by the wave without changing value as the wave propagates (and X moves). An interpretation of $\partial_\alpha D^\alpha = 0$ as a statement of the wave's dispersion relation $\omega = |\mathbf{k}|$ follows simply from this picture, as detailed in the text.

radiation field [11] can be expressed in manifestly electric-magnetic symmetric forms *in general* as

$$\begin{aligned}
 \mathcal{S} &= \int \int \int_{-\infty}^{\infty} i\tilde{\alpha} \times \tilde{\alpha}^* d^3\mathbf{k} \\
 &= \int \int \int_{-\infty}^{\infty} \mathbf{E}^\perp \times \mathbf{A}^\perp d^3\mathbf{r} \\
 &= \int \int \int_{-\infty}^{\infty} \frac{1}{2} \left(\mathbf{E}^\perp \times \mathbf{A}^\perp + \mathbf{B} \times \mathbf{C}^\perp \right) d^3\mathbf{r}, \tag{3.104}
 \end{aligned}$$

$$\begin{aligned}
 \mathcal{L} &= \int \int \int_{-\infty}^{\infty} i\tilde{\alpha}_{(a)} (\mathbf{k} \times \nabla_{\mathbf{k}}) \tilde{\alpha}_{(a)}^* d^3\mathbf{k} \\
 &= \int \int \int_{-\infty}^{\infty} E_{(a)}^\perp (\mathbf{r} \times \nabla) A_{(a)}^\perp d^3\mathbf{r} \\
 &= \int \int \int_{-\infty}^{\infty} \frac{1}{2} \left[E_{(a)}^\perp (\mathbf{r} \times \nabla) A_{(a)}^\perp + B_{(a)}^\perp (\mathbf{r} \times \nabla) C_{(a)}^\perp \right] d^3\mathbf{r}, \tag{3.105}
 \end{aligned}$$

which strengthens our resolve that we did indeed identify a meaningful definition of \mathbf{C}^\perp in particular in the presence of charge in §2.3: the equalities relating the second and third lines of (3.104) and of

(3.105) would *not* have held had we defined \mathbf{C}^\perp in another manner such as $\mathbf{B} = -\dot{\mathbf{C}}^\perp$, for example. Moreover, if these equalities did not exist, we would have been forced to conclude, somewhat unsatisfactorily, that the familiar ‘ \mathbf{E}, \mathbf{A} ’ forms of \mathcal{S} and \mathcal{L} were more fundamental than the manifestly electric-magnetic symmetric ‘ $\mathbf{E}, \mathbf{B}, \mathbf{A}, \mathbf{C}$ ’ forms, as the latter would have *only* been appropriate in the strict absence of charge by virtue of the equalities linking the first and second lines of (3.9) and of (3.10) within that domain. As the \mathbf{E}, \mathbf{A} forms and the $\mathbf{E}, \mathbf{B}, \mathbf{A}, \mathbf{C}$ forms of \mathcal{S} and \mathcal{L} are, in fact, equivalent, their properties, couplings to charge etc [11, 24, 59, 60] are identical. We meet with similarly pleasing results elsewhere in the fundamental description of the angular momentum of light. In particular, we find that the helicity $\mathcal{H} = \mathcal{H}(t)$ of the radiation field⁹ takes the form

$$\begin{aligned}\mathcal{H} &= \iiint_{\infty} i \tilde{\alpha} \times \tilde{\alpha}^* \cdot \hat{\mathbf{k}} d^3\mathbf{k} \\ &= \iiint_{\infty} \frac{1}{2} (\mathbf{A}^\perp \cdot \mathbf{B} - \mathbf{C}^\perp \cdot \mathbf{E}^\perp) d^3\mathbf{r},\end{aligned}\tag{3.106}$$

where the first line seen in (3.106) should be compared with the first line seen in (3.104). Interestingly, the coupling of \mathcal{H} to charge:

$$\begin{aligned}\dot{\mathcal{H}} &= \iiint_{\infty} \mathbf{J} \cdot \mathbf{C}^\perp d^3\mathbf{r} \\ &= \sum_{n=1}^N q_n \dot{\mathbf{r}}_n \cdot \mathbf{C}^\perp(\mathbf{r}_n, t),\end{aligned}\tag{3.107}$$

is centred upon \mathbf{C}^\perp .

Pleasingly, the analogy drawn in §3.3.7 between helicity, spin etc and energy, linear momentum etc holds even in the presence of charge: the former properties of the radiation field, as well as their couplings to charge, are transformed into the latter and their couplings to charge under the superficial mapping

$$\begin{aligned}\mathbf{A}^\perp &\rightarrow \mathbf{B} \\ \mathbf{C}^\perp &\rightarrow -\mathbf{E}^\perp \\ \mathbf{E}^\perp &\rightarrow \mathbf{E}^\perp \\ \mathbf{B} &\rightarrow \mathbf{B},\end{aligned}\tag{3.108}$$

⁹ \mathcal{H} is a mere rotational pseudoscalar as opposed to a Lorentz pseudoscalar: it only attains a Lorentz-invariant status in the strict absence of charge. Superficially, at least, this can be related to the apparent impossibility of constructing a four-pseudovector from Θ and \mathbf{C} .

which, for example, transforms the equation (3.107) expressing the coupling of \mathcal{H} to charge into

$$\begin{aligned} \frac{d}{dt} \iiint_{\infty} \frac{1}{2} (\mathbf{E}^{\perp} \cdot \mathbf{E}^{\perp} + \mathbf{B} \cdot \mathbf{B}) d^3\mathbf{r} &= - \iiint_{\infty} \mathbf{J} \cdot \mathbf{E}^{\perp} d^3\mathbf{r} \\ &= - \sum_{n=1}^N q_n \dot{\mathbf{r}}_n \cdot \mathbf{E}^{\perp}(\mathbf{r}_n, t), \end{aligned} \quad (3.109)$$

expressing the coupling of the energy of the radiation field to charge.

Naturally, the operator $\hat{\mathbf{C}}^{\perp}$ representing \mathbf{C}^{\perp} also plays the expected role in the fundamental description of the angular momentum of light. We find, for example, that the operator $\hat{\mathcal{H}}$ representing \mathcal{H} takes the form

$$\begin{aligned} \hat{\mathcal{H}} &= \sum_{\mathbf{k}} \sum_{\sigma} \sigma \hbar \hat{n}_{\mathbf{k}\sigma} \\ &= \iiint_V \frac{1}{2} (\hat{\mathbf{A}}^{\perp} \cdot \hat{\mathbf{B}} - \hat{\mathbf{C}}^{\perp} \cdot \hat{\mathbf{E}}^{\perp}) d^3\mathbf{r}, \end{aligned} \quad (3.110)$$

describing a helicity of $\pm\hbar$ per circularly polarised plane-wave-mode photon of wavevector \mathbf{k} and polarisation parameter $\sigma = \pm 1$. Multiple formulations of quantum electrodynamics exist that are equivalent in their physical predictions and considerable care must be taken, of course, in extending to them such results. To illustrate this, suppose now that we work not in the minimal coupling formalism but rather in the multipolar formalism [11, 12]. If we *insist* on identifying a helicity of $\pm\hbar$ per circularly polarised plane-wave-mode photon of wavevector \mathbf{k} and polarisation parameter $\sigma = \pm 1$, the operator $\hat{\mathcal{H}}' \neq \hat{\mathcal{H}}$ representing the helicity $\mathcal{H}' \neq \mathcal{H}$ then assumes the form

$$\begin{aligned} \hat{\mathcal{H}}' &= \sum_{\mathbf{k}} \sum_{\sigma} \sigma \hbar \hat{n}'_{\mathbf{k}\sigma} \\ &= \iiint_V \frac{1}{2} (\hat{\mathbf{A}}^{\perp} \cdot \hat{\mathbf{B}} - \hat{\mathbf{C}}'^{\perp} \cdot \hat{\mathbf{D}}^{\perp}) d^3\mathbf{r}, \end{aligned} \quad (3.111)$$

with $\hat{n}'_{\mathbf{k}\sigma}$ the number operator for a circularly polarised plane-wave-mode photon of wavevector \mathbf{k} and polarisation parameter σ , $\hat{\mathbf{D}}^{\perp} = \hat{\mathbf{D}}^{\perp}(\mathbf{r})$ the operator representing the solenoidal piece \mathbf{D}^{\perp} of the electric displacement field \mathbf{D} and the operator $\hat{\mathbf{C}}'^{\perp} = \hat{\mathbf{C}}'^{\perp}(\mathbf{r})$ defined such that $\hat{\mathbf{D}}^{\perp} = -\nabla \times \hat{\mathbf{C}}'^{\perp}$. Although the first line seen in (3.111) is identical in form to that seen in (3.110), the second line *differs* from that seen in (3.110) because the notion of a photon in the multipolar formalism differs from that in the minimal coupling formalism [11, 12].

3.8 Discussion

We have explored the fundamental description in the theory of electrodynamics of the angular momentum of light. We have recognised in particular that light possesses an infinite collection of intrinsic rotation angular momenta in addition to spin, the members of which are sensitive to photon *helicity*, with helicity itself lying at very heart of the collection. In addition, we have pursued analogous ideas

for the extrinsic and quasi-extrinsic rotation angular momentum of light, as well as the boost angular momentum of light. Some of the relations between the angular momenta that we have met are depicted in figure 3.6.

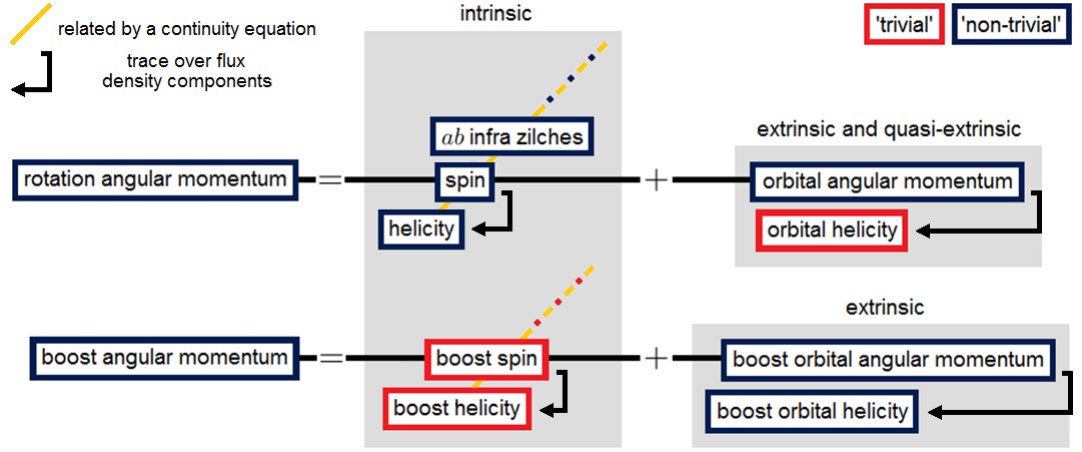


Figure 3.6: An attempt to categorise the various angular momenta possessed by light, as well as indicate some of the relationships between them. By 'trivial', we mean here that the total angular momentum vanishes (although the associated density and flux density are non-vanishing in general).

There remains much to be explored, of course. I would like to study the local description of orbital angular momentum in more detail, with a focus upon the subtle interplay between its extrinsic and quasi-intrinsic components. Moreover, I would like to better understand the boost angular momentum of light which remains rather neglected, it seems, relative to the rotation angular momentum of light. These are tasks for future research.

Chapter 4

Noether's Theorem and Electric-Magnetic Democracy

4.1 Introduction

Ultimately, quantities such as energy, linear momentum and angular momentum are important because they are conserved. Conservation laws are important in turn because they apparently constrain the evolution of a system and aid in calculations: Newton's laws of motion, for example, can be regarded as statements of linear momentum conservation. The idea of a conservation law can be traced back at least as far as Descartes, who suggested (incorrectly) that the product of 'size' and speed is conserved in collisions between material bodies [36].

In her well known (first) theorem, Noether established that continuous symmetries inherent in the equations of motion governing a system are associated with conservation laws which the system respects [104, 105]. In electrodynamics, Noether's theorem was first applied by Bessel-Hagen [106] and much has been written in this context since. There remains a great deal that is not understood, however, and, in the present chapter, we approach this subject from the perspective of electric-magnetic democracy. In particular, this lends us a deeper understanding of the angular momenta that we identified heuristically in §3: the conservation of these in the strict absence of charge reflect the myriad ways in which it is possible to rotate light that is freely propagating. The text is based primarily upon my research paper [107].

4.2 Formalism

4.2.1 Noether's theorem: qualitative description

The *quantitative* formulation of Noether's theorem requires some rather complicated mathematics, which tends to obscure the relatively simple ideas involved. Let us begin, therefore, with a *qualitative* description of Noether's theorem in the context of electrodynamics.

Suppose initially that the trajectories \mathbf{r}_n of the particles as well as the electric field \mathbf{E} and the mag-

netic flux density \mathbf{B} evolve in accord with the Newton-Einstein-Lorentz equation (1.3) and Maxwell's equations (1.4)-(1.7). Now imagine actively performing the infinitesimal transformation

$$\begin{aligned}\mathbf{r}_n &\rightarrow \mathbf{r}'_n = \mathbf{r}_n + \delta\mathbf{r}_n \\ \mathbf{E} &\rightarrow \mathbf{E}' = \mathbf{E} + \delta\mathbf{E} \\ \mathbf{B} &\rightarrow \mathbf{B}' = \mathbf{B} + \delta\mathbf{B}.\end{aligned}\tag{4.1}$$

If we choose the infinitesimal changes $\delta\mathbf{r}_n$, $\delta\mathbf{E}$ and $\delta\mathbf{B}$ such that the transformed trajectories \mathbf{r}'_n of the particles, the transformed electric field \mathbf{E}' and the transformed magnetic flux density \mathbf{B}' also satisfy (1.3)-(1.7), we say that (4.1) is an infinitesimal *symmetry* transformation. Noether's theorem associates conservation laws with the existence of these symmetry transformations [104, 105].

There exist ten continuous symmetry transformations in electrodynamics, namely translations in time, translations in space, circular rotations in space and boosts, the latter being hyperbolic rotations in spacetime, of course. The conservation laws traditionally associated with these through Noether's theorem pertain to energy, linear momentum, rotation angular momentum and boost angular momentum, as was first demonstrated (for light that is freely propagating) by Bessel-Hagen [106]. In addition, the gauge invariance of \mathbf{E} and \mathbf{B} is usually associated with the conservation of charge [8, 108]. There exist other symmetries in electrodynamics, of course, such as the invariance of (1.3)-(1.7) under time reversal and parity reversal [2, 25]. Being discrete rather than continuous, such symmetry transformations cannot obviously be brought into an infinitesimal form so as to be investigated using Noether's theorem, however [104, 105].

Let us now focus our attention upon light that is propagating freely in the strict absence of charge. As we will demonstrate in what follows, Maxwell's equations (1.68)-(1.71) then exhibit an *infinite* number of continuous symmetries and associated conservation laws of distinct character.

4.2.2 The standard Lagrangian density

In modern terms, Fermat's principle states that the path taken by a ray of light in geometrical optics is such that the time that elapses is 'stationary' with respect to variations in this path [27, 105]. Hamilton expressed this using the language of variational calculus [109] and subsequently expanded his work to the study of the dynamics of systems of particles [110, 111], thus elucidating the principle that now bears his name [112]. As a precursor to our quantitative formulation of Noether's theorem, let us begin now by reviewing Hamilton's principle, as it is usually applied to light that is propagating freely in the strict absence of charge.

Suppose that the form of the light is known at times $t = t_1$ and $t = t_2$ for all positions \mathbf{r} and as $|\mathbf{r}| \rightarrow \infty$ for $t_1 \leq t \leq t_2$. An action S of the light is then defined as

$$S = \int_{t_1}^{t_2} L dt\tag{4.2}$$

with L a Lagrangian of the light, related in turn to a Lagrangian density \mathcal{L} as

$$L = \int \int \int_{\infty} \mathcal{L} d^3 \mathbf{r}. \quad (4.3)$$

Hamilton's principle states that the true dynamical path followed by the light for $t_1 \leq t \leq t_2$ is such that S is stationary with respect to neighbouring paths [110–112]. This allows us to derive the equations of motion governing the light, provided \mathcal{L} is itself chosen suitably. The most commonly employed choice is, perhaps [2, 10, 14, 113],

$$\mathcal{L}_0 = -\frac{1}{4} (\partial_\alpha A_\beta - \partial_\beta A_\alpha) (\partial^\alpha A^\beta - \partial^\beta A^\alpha), \quad (4.4)$$

with the components of A^α taken to be the generalised coordinates of the light, their first derivatives constituting generalised velocities¹ so that $\mathcal{L}_0 = \mathcal{L}_0(A_\alpha, \partial_\beta A_\alpha)$. We refer to \mathcal{L}_0 as the *standard* Lagrangian density [11]. It is due to Schwarzschild [11, 114]. Hamilton's principle is applied by supposing that A^α follows the true dynamical path and considering a small deviation²

$$A^\alpha \rightarrow A'^\alpha = A^\alpha + \delta A^\alpha, \quad (4.5)$$

with the infinitesimal four vector δA^α satisfying $\delta A^\alpha(\mathbf{r}, t_1) = \delta A^\alpha(\mathbf{r}, t_2) = 0$ for all \mathbf{r} and $\delta A^\alpha(\mathbf{r}, t) \rightarrow 0$ as $|\mathbf{r}| \rightarrow \infty$ for $t_1 \leq t \leq t_2$. The corresponding deviation $\delta \mathcal{L}_0 = \mathcal{L}'_0 - \mathcal{L}_0$ in \mathcal{L}_0 is

$$\begin{aligned} \delta \mathcal{L}_0 &= \frac{\partial \mathcal{L}_0}{\partial A_\alpha} \delta A_\alpha + \frac{\partial \mathcal{L}_0}{\partial (\partial_\beta A_\alpha)} \delta (\partial_\beta A_\alpha) \\ &= \left\{ \frac{\partial \mathcal{L}_0}{\partial A_\alpha} + \partial_\beta \left[\frac{\partial \mathcal{L}_0}{\partial (\partial_\beta A_\alpha)} \right] \right\} \delta A_\alpha - \partial_\beta \left[\frac{\partial \mathcal{L}_0}{\partial (\partial_\beta A_\alpha)} \delta A_\alpha \right] \end{aligned} \quad (4.6)$$

and the corresponding deviation $\delta S_0 = S'_0 - S_0$ in S_0 follows as

$$\delta S_0 = \int_{t_1}^{t_2} \int \int \int_{\infty} \left\{ \frac{\partial \mathcal{L}_0}{\partial A_\alpha} + \partial_\beta \left[\frac{\partial \mathcal{L}_0}{\partial (\partial_\beta A_\alpha)} \right] \right\} \delta A_\alpha d^3 \mathbf{r} dt, \quad (4.7)$$

which must vanish for all suitable δA^α , by assumption. Thus, we arrive at the Euler-Lagrange equations:

$$\partial_\beta \left[\frac{\partial \mathcal{L}_0}{\partial (\partial_\beta A_\alpha)} \right] = \frac{\partial \mathcal{L}_0}{\partial A_\alpha}, \quad (4.8)$$

which govern the light for $t_1 \leq t \leq t_2$. Explicit calculation reveals that these (4.8) are

$$\partial_\beta F^{\alpha\beta} = 0, \quad (4.9)$$

which is (1.31) with $J^\alpha = 0$. Thus, \mathcal{L}_0 has, through application of Hamilton's principle, provided us explicitly with four of the eight Maxwell equations as written in the strict absence of charge. The remaining four (1.32) are satisfied *automatically*, of course, by virtue of the definition $F^{\alpha\beta} = \partial^\alpha A^\beta - \partial^\beta A^\alpha$,

¹Strictly speaking, the first *time* derivatives \dot{A}^α of A^α are the generalised velocities whilst the appearance of the first *spatial* derivatives $\partial_a A^\alpha$ of A^α in \mathcal{L}_0 reflects the continuous nature of light. Interestingly, \dot{A}^0 does not actually appear [11]. Note that \mathbf{r} is not subjected to variation but rather is regarded as a continuous label [11].

²Our independent variation of the A^α precludes the imposition of a gauge [11, 14].

as described in §1.2.2.

In general, it is the equations of motion governing a system that are directly verified in experiment, not an action, Lagrangian or indeed Lagrangian density. Although the latter are sometimes regarded as being more fundamental, the fact should be borne in mind that they are postulated to *yield* the equations of motion and, as such, are not unique.

4.2.3 The electric-magnetic Lagrangian density

The research described in the present chapter was motivated by a desire to understand the implications of electric-magnetic democracy in the context of Noether's theorem. Surprisingly, however, we find that the standard Lagrangian density \mathcal{L}_0 does not retain its form under a Heaviside-Larmor rotation (2.1). This is, perhaps, a reflection of the fact that \mathcal{L}_0 is defined solely in terms of a *magnetic* potential A^α . Whilst this peculiar characteristic does not give rise to any *fundamental* difficulties, it encourages us nevertheless to add half of \mathcal{L}_0 to half of the analogous electric form, obtaining

$$\begin{aligned}\mathcal{L} = & -\frac{1}{8}(\partial_\alpha A_\beta - \partial_\beta A_\alpha)(\partial^\alpha A^\beta - \partial^\beta A^\alpha) \\ & -\frac{1}{8}(\partial_\alpha C_\beta - \partial_\beta C_\alpha)(\partial^\alpha C^\beta - \partial^\beta C^\alpha).\end{aligned}\quad (4.10)$$

Naïvely, we might now consider the eight components of A^α and C^α to be the generalised coordinates of the light, their first derivatives constituting generalised velocities. There is, however, a subtle but important point that must be appreciated here, one that stems from the problem of overdetermination. If we identify A^α and C^α as potentials a priori, we find that \mathcal{L} vanishes, by virtue of the fact that $G^{\alpha\beta} = \epsilon^{\alpha\beta\gamma\delta} F_{\gamma\delta}/2$.

To proceed, suppose initially that we attach no physical interpretation to the four vector A^α or the four pseudovector C^α except that their dimensions are such that \mathcal{L} in turn has the dimensions of an energy per unit volume. Considering A^α and C^α to be *independent* of each other and applying Hamilton's principle, we then obtain eight Euler-Lagrange equations:

$$\partial_\beta (\partial^\alpha A^\beta - \partial^\beta A^\alpha) = 0, \quad (4.11)$$

$$\partial_\beta (\partial^\alpha C^\beta - \partial^\beta C^\alpha) = 0. \quad (4.12)$$

Restricting our attention now to the solutions of (4.11) and (4.12) for which

$$\partial^\alpha C^\beta - \partial^\beta C^\alpha = \frac{1}{2}\epsilon^{\alpha\beta\gamma\delta}(\partial_\gamma A_\delta - \partial_\delta A_\gamma), \quad (4.13)$$

we *can* identify A^α and C^α as potentials and thus make contact with electrodynamics as $F^{\alpha\beta} = \partial^\alpha A^\beta - \partial^\beta A^\alpha = -\epsilon^{\alpha\beta\gamma\delta}(\partial_\gamma C_\delta - \partial_\delta C_\gamma)/2$ and $G^{\alpha\beta} = \epsilon^{\alpha\beta\gamma\delta}(\partial_\gamma A_\delta - \partial_\delta A_\gamma)/2 = \partial^\alpha C^\beta - \partial^\beta C^\alpha$, in which case (4.11) and (4.12) are the complete set of Maxwell equations as written in the strict absence of charge and (4.13) is $G^{\alpha\beta} = \epsilon^{\alpha\beta\gamma\delta} F_{\gamma\delta}/2$. This should be contrasted with the fact that \mathcal{L}_0 only provides us with four of the eight Maxwell equations explicitly, the remaining four holding

implicitly.

We refer to \mathcal{L} as the *electric-magnetic* Lagrangian density. Like \mathcal{L}_0 , \mathcal{L} is a Lorentz scalar field with the dimensions of an energy per unit volume and possesses a form that is insensitive to the gauge of A^α and analogously for C^α . The forms of the Lagrangian L and action S associated with \mathcal{L} differ from those considered by Zwanziger [6, 7], Schwinger [5] and Drummond [71, 72]. Moreover, our treatment of the eight components of A^α and C^α as the generalised coordinates of the light differs from the approaches taken by Schwinger [5] and Drummond [71, 72], who treat various components of the potentials and the *field* itself as quantities to be subjected to independent variations. The form exhibited by \mathcal{L} has, however, been considered briefly by Rañada [115]. At the time of publishing the research described in the present chapter [107], the form of \mathcal{L} was also recognised by Bliokh, Bekshaev and Nori [116].

4.2.4 Noether's theorem: quantitative derivation

We now derive a form of Noether's theorem based upon \mathcal{L} . Suppose that A^α and C^α satisfy Maxwell's equations as written in the strict absence of charge (4.11) and (4.12) and imagine actively performing the infinitesimal transformation

$$\begin{aligned} A^\alpha &\rightarrow A'^\alpha = A^\alpha + \delta A^\alpha \\ C^\alpha &\rightarrow C'^\alpha = C^\alpha + \delta C^\alpha \end{aligned} \quad (4.14)$$

where, *at present*, we make no assumptions about the four vector δA^α or the four pseudovector δC^α except that they are infinitesimal. Standard calculus, together with Maxwell's equations as written in the strict absence of charge (4.11) and (4.12), gives us an expression for the corresponding change $\delta\mathcal{L} = \mathcal{L}' - \mathcal{L}$ in \mathcal{L} :

$$\begin{aligned} \delta\mathcal{L} &= \frac{\partial\mathcal{L}}{\partial(\partial_\beta A_\alpha)} \delta(\partial_\beta A_\alpha) + \frac{\partial\mathcal{L}}{\partial(\partial_\beta C_\alpha)} \delta(\partial_\beta C_\alpha) \\ &= \frac{\partial\mathcal{L}}{\partial(\partial_\beta A_\alpha)} \partial_\beta \delta A_\alpha + \frac{\partial\mathcal{L}}{\partial(\partial_\beta C_\alpha)} \partial_\beta \delta C_\alpha \\ &= \partial_\beta \left[\frac{\partial\mathcal{L}}{\partial(\partial_\beta A_\alpha)} \delta A_\alpha + \frac{\partial\mathcal{L}}{\partial(\partial_\beta C_\alpha)} \delta C_\alpha \right] - \partial_\beta \left[\frac{\partial\mathcal{L}}{\partial(\partial_\beta A_\alpha)} \right] \delta A_\alpha - \partial_\beta \left[\frac{\partial\mathcal{L}}{\partial(\partial_\beta C_\alpha)} \right] \delta C_\alpha \\ &= \partial_\beta \left[\frac{1}{2} \left(F^{\alpha\beta} \delta A_\alpha + G^{\alpha\beta} \delta C_\alpha \right) \right] - \frac{1}{2} \partial_\beta F^{\alpha\beta} \delta A_\alpha - \frac{1}{2} \partial_\beta G^{\alpha\beta} \delta C_\alpha \\ &= \partial_\beta \left[\frac{1}{2} \left(F^{\alpha\beta} \delta A_\alpha + G^{\alpha\beta} \delta C_\alpha \right) \right]. \end{aligned} \quad (4.15)$$

If the transformation seen in (4.14) leaves \mathcal{L} *invariant* ($\delta\mathcal{L} = 0$), we say that (4.14) is an infinitesimal *symmetry* transformation. Its associated local conservation law then follows from (4.15) as

$$\partial_\beta \left[\frac{1}{2} \left(F^{\alpha\beta} \delta A_\alpha + G^{\alpha\beta} \delta C_\alpha \right) \right] = 0. \quad (4.16)$$

This is the form of Noether's theorem that we adopt in the present chapter. Note that (4.16) holds regardless of any gauge imposed upon A^α or analogously for C^α ; a reflection in turn of the fact that \mathcal{L} possesses a form that is insensitive to the imposition of a gauge upon A^α or analogously for C^α .

At the time of publishing the research described in the present chapter [107], Bliokh, Bekshaev and Nori [116] also published a Noether investigation on the basis of \mathcal{L} . Acknowledgement of both magnetic and electric potentials has also led Drummond [71, 72] and Anco and The [43] to undertake related investigations.

4.2.5 Some important subtleties

For arbitrary choices of δA^α and δC^α , the transformation seen in (4.14) is meaningless, in general. We demand, in fact, that δA^α and δC^α be related such that the transformed quantities A'^α and C'^α satisfy

$$\partial^\alpha C'^\beta - \partial^\beta C'^\alpha = \frac{1}{2} \epsilon^{\alpha\beta\gamma\delta} (\partial_\gamma A'_\delta - \partial_\delta A'_\gamma), \quad (4.17)$$

thus staying faithful to electrodynamics. It will be noticed that *all* such transformations constitute symmetries of Maxwell's equations as written in the strict absence of charge (4.11) and (4.12), which are satisfied automatically when the field is defined consistently in terms of two potentials, as discussed in §2.2. In addition, $\mathcal{L} = \mathcal{L}' = \delta\mathcal{L} = 0$ for all such transformations. Thus, *all* symmetries of Maxwell's equations as written in the strict absence of charge (4.11) and (4.12) are also *strict* ($\delta\mathcal{L} = 0$) symmetries of \mathcal{L} and vice-versa, a most pleasing correspondence that does *not* exist between symmetries of the former and *strict* ($\delta\mathcal{L}_0 = 0$) symmetries of \mathcal{L}_0 . Thus, our employment of \mathcal{L} rather than \mathcal{L}_0 enables us to carry out a Noetherian investigation with unprecedented simplicity. We emphasise nevertheless that the same results can be deduced using \mathcal{L}_0 , albeit at the expense of considerable effort in some cases. We suggest that \mathcal{L} be viewed as an alternative to \mathcal{L}_0 , rather than a replacement; they lead to the same dynamics and hence the same conservation laws.

Here, let us highlight a subtle point of general interest. Although the same mathematical manipulations are employed in deriving Euler-Lagrange equations and in deriving Noether's theorem, the motivations for employing them differ: in the first context, coordinate changes (in the present case δA^α and δC^α) are chosen specifically so as to *violate* the Euler-Lagrange equations whereas in the second context, coordinate changes (δA^α and δC^α) are chosen specifically so as to *respect* the Euler-Lagrange equations.

4.2.6 Uniqueness and the canonical form

We now have all the tools at our disposal to begin our Noetherian investigation. Before doing so, allow us however to briefly consider questions of uniqueness and thus introduce the canonical form.

A *given* infinitesimal symmetry transformation

$$\begin{aligned}\mathbf{E} &\rightarrow \tilde{\mathbf{E}} = \mathbf{E} + \delta\mathbf{E} \\ \mathbf{B} &\rightarrow \tilde{\mathbf{B}} = \mathbf{B} + \delta\mathbf{B}\end{aligned}\tag{4.18}$$

of the *field* can be invoked at the level of the *potentials* in *multiple* ways. Looking at one of these

$$\begin{aligned}\Phi &\rightarrow \tilde{\Phi} = \Phi + \delta\Phi \\ \Theta &\rightarrow \tilde{\Theta} = \Theta + \delta\Theta \\ \mathbf{A}^{\parallel} &\rightarrow \tilde{\mathbf{A}}^{\parallel} = \mathbf{A}^{\parallel} + \delta\mathbf{A}^{\parallel} \\ \mathbf{A}^{\perp} &\rightarrow \tilde{\mathbf{A}}^{\perp} = \mathbf{A}^{\perp} + \delta\mathbf{A}^{\perp} \\ \mathbf{C}^{\parallel} &\rightarrow \tilde{\mathbf{C}}^{\parallel} = \mathbf{C}^{\parallel} + \delta\mathbf{C}^{\parallel} \\ \mathbf{C}^{\perp} &\rightarrow \tilde{\mathbf{C}}^{\perp} = \mathbf{C}^{\perp} + \delta\mathbf{C}^{\perp},\end{aligned}\tag{4.19}$$

we observe, however, that

$$\begin{aligned}\delta\mathbf{E} &= -\delta\dot{\mathbf{A}}^{\perp} = -\nabla \times \delta\mathbf{C}^{\perp}, \\ \delta\mathbf{B} &= \nabla \times \delta\mathbf{A}^{\perp} = -\delta\dot{\mathbf{C}}^{\perp}.\end{aligned}\tag{4.20}$$

Evidently $\delta\Phi$, $\delta\Theta$, $\delta\mathbf{A}^{\parallel}$ and $\delta\mathbf{C}^{\parallel}$ make vanishing contributions to $\delta\mathbf{E}$ and $\delta\mathbf{B}$ and the latter are, therefore, determined entirely by $\delta\mathbf{A}^{\perp}$ and $\delta\mathbf{C}^{\perp}$. Conversely, $\delta\mathbf{A}^{\perp}$ and $\delta\mathbf{C}^{\perp}$ are uniquely defined for a given $\delta\mathbf{E}$ and $\delta\mathbf{B}$ but $\delta\Phi$, $\delta\Theta$, $\delta\mathbf{A}^{\parallel}$ and $\delta\mathbf{C}^{\parallel}$ are not and can take any form corresponding to an infinitesimal gauge transformation. Consequently, many local conservation laws (from Noether's theorem (4.16));

$$\frac{\partial}{\partial t} \left[\frac{1}{2} (-\mathbf{E} \cdot \delta\mathbf{A} - \mathbf{B} \cdot \delta\mathbf{C}) \right] + \nabla \cdot \left[\frac{1}{2} (-\mathbf{E}\delta\Phi - \mathbf{B}\delta\Theta + \mathbf{B} \times \delta\mathbf{A} - \mathbf{E} \times \delta\mathbf{C}) \right] = 0, \tag{4.21}$$

of different appearance exist for a given $\delta\mathbf{E}$ and $\delta\mathbf{B}$. We suggest, however, that the local conservation law

$$\frac{\partial}{\partial t} \left[\frac{1}{2} (-\mathbf{E} \cdot \delta\mathbf{A}^{\perp} - \mathbf{B} \cdot \delta\mathbf{C}^{\perp}) \right] + \nabla \cdot \left[\frac{1}{2} (\mathbf{B} \times \delta\mathbf{A}^{\perp} - \mathbf{E} \times \delta\mathbf{C}^{\perp}) \right] = 0 \tag{4.22}$$

obtained for $\delta\Phi = \delta\Theta = \delta\mathbf{A}^{\parallel} = \delta\mathbf{C}^{\parallel} = 0$ embodies the very *core* of the infinitesimal symmetry transformation (4.18) and we refer to it as the *canonical* form. It is pleasing, perhaps, to note that both (4.21) and (4.22) yield the same global conservation law

$$\iiint_{\infty} \frac{1}{2} (-\mathbf{E} \cdot \delta\mathbf{A}^{\perp} - \mathbf{B} \cdot \delta\mathbf{C}^{\perp}) d^3\mathbf{r} = \text{constant}.\tag{4.23}$$

Looking at (4.22) and indeed (4.23), it may be tempting to identify 'unique' densities and flux densities directly from

$$\frac{1}{2} (-\mathbf{E} \cdot \delta\mathbf{A}^{\perp} - \mathbf{B} \cdot \delta\mathbf{C}^{\perp}) \quad \text{and} \quad \frac{1}{2} (\mathbf{B} \times \delta\mathbf{A}^{\perp} - \mathbf{E} \times \delta\mathbf{C}^{\perp}). \tag{4.24}$$

Nevertheless, we must emphasise that Noether's theorem (4.16) does *not* yield densities or flux densities explicitly and that the identification of such quantities is, it seems, not unique, *even* given the canonical form. Indeed, we may have identified a canonical form of different appearance had we chosen to work with a different but equally valid Lagrangian density, for example \mathcal{L}_0 .

4.3 Local symmetry transformations and their associated conservation laws

In the present section, we consider local symmetry transformations, in which the changes $\delta\mathbf{E}$ and $\delta\mathbf{B}$ in the electric field \mathbf{E} and the magnetic flux density \mathbf{B} depend exclusively upon the latter and perhaps their derivatives at the same time t and position \mathbf{r} . These symmetry transformations can be expressed simply using the language of tensor and pseudotensor calculus. We exploit the freedom described in §4.2.6 to obtain associated continuity equations that are themselves manifestly covariant and depend only upon the electromagnetic field tensor $F^{\alpha\beta}$, the dual electromagnetic field tensor $G^{\alpha\beta}$ and their various partial derivatives, with but two exceptions in which a magnetic potential four vector A^α and an electric potential four pseudovector C^α appear explicitly. Such forms are sometimes referred to as being *mechanical*.

4.3.1 Heaviside-Larmor rotations and the conservation of helicity

The invariance in form of Maxwell's equations as written in the strict absence of charge (4.11) and (4.12) under a Heaviside-Larmor rotation (2.1) was, perhaps, the *first*³ symmetry identified in the theory of electrodynamics and it seems natural, therefore, to begin our investigation here.

We invoke an infinitesimal Heaviside-Larmor rotation

$$\begin{aligned} F^{\alpha\beta} &\rightarrow F'^{\alpha\beta} = F^{\alpha\beta} + \theta G^{\alpha\beta} \\ G^{\alpha\beta} &\rightarrow G'^{\alpha\beta} = G^{\alpha\beta} - \theta F^{\alpha\beta} \end{aligned} \quad (4.25)$$

as

$$\begin{aligned} A^\alpha &\rightarrow A'^\alpha = A^\alpha + \theta C^\alpha \\ C^\alpha &\rightarrow C'^\alpha = C^\alpha - \theta A^\alpha, \end{aligned} \quad (4.26)$$

with the angle θ infinitesimal. It then follows immediately from Noether's theorem (4.16) that

$$\partial_\alpha h^\alpha = 0 \quad \text{with} \quad h^\alpha = \frac{1}{2} \left(A_\beta G^{\alpha\beta} - C_\beta F^{\alpha\beta} \right), \quad (4.27)$$

where we have made use of the fact that $\theta \neq 0$. This continuity equation (4.27) embodies the conservation of helicity: its associated canonical form coincides with the helicity continuity equation (3.44) which we originally identified heuristically. For a single plane wave, a Heaviside-Larmor rota-

³If we exclude gauge freedom, which was recognised by Maxwell himself [19].

tion (2.1) literally rotates the electric field vectors and magnetic flux density pseudovectors about the direction of propagation through θ [37, 52]: see figure 4.1. It seems natural, perhaps, that such a

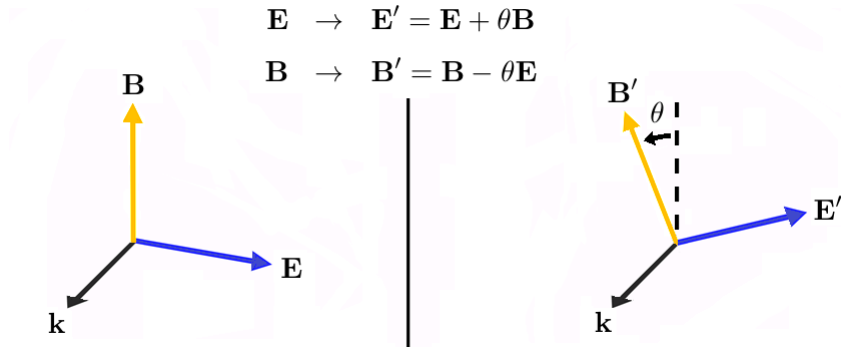


Figure 4.1: The effect of an infinitesimal Heaviside-Larmor rotation (4.25) on a single plane wave of wavevector \mathbf{k} .

symmetry transformation should be associated with the conservation of helicity. The association of Heaviside-Larmor rotations with the conservation of helicity was recognised first by Calkin [70] (see also [6, 43, 71–73, 75–77]).

This is not yet the end of our story. Consider now the infinitesimal symmetry transformation

$$\begin{aligned} F^{\alpha\beta} &\rightarrow F'^{\alpha\beta} = F^{\alpha\beta} + \phi F^{\alpha\beta} \\ G^{\alpha\beta} &\rightarrow G'^{\alpha\beta} = G^{\alpha\beta} + \phi G^{\alpha\beta} \end{aligned} \quad (4.28)$$

with the angle ϕ infinitesimal. Just as (4.25) is, for a single plane wave, an infinitesimal rotation of the electric field vectors and magnetic flux density pseudovectors about the direction of propagation through θ , (4.28) is an infinitesimal boost of the electric field vectors and magnetic flux density pseudovectors in the direction of propagation with rapidity ϕ , leaving the spacetime distribution of the wave unchanged: see figure 4.2. This interpretation also holds for the finite form of (4.28). Thus,

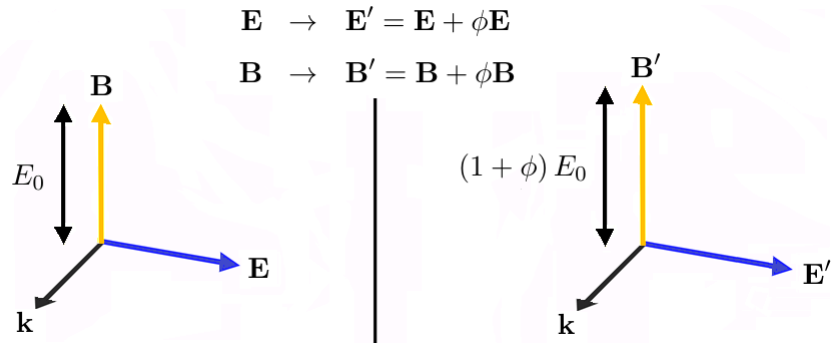


Figure 4.2: The effect of an infinitesimal boost helicity symmetry transformation (4.28) on a single plane wave of amplitude E_0 and wavevector \mathbf{k} .

(4.25) and (4.28) are ‘partners’. We invoke (4.28) as

$$\begin{aligned} A^\alpha \rightarrow A'^\alpha &= A^\alpha + \phi A^\alpha \\ C^\alpha \rightarrow C'^\alpha &= C^\alpha + \phi C^\alpha \end{aligned} \quad (4.29)$$

and are led immediately by Noether’s theorem (4.16) to the continuity equation

$$\partial_\alpha d^\alpha = 0 \quad \text{with} \quad d^\alpha = \frac{1}{2} \left(A_\beta F^{\beta\alpha} + C_\beta G^{\beta\alpha} \right), \quad (4.30)$$

which embodies the conservation of boost helicity: its canonical form coincides with the boost helicity continuity equation (3.87) which we originally identified heuristically. As we observed in §3.6.1, boost helicity is a trivial quantity in that the boost helicity \mathcal{D} itself vanishes. Related observations have been made by Fushchich and Nikitin [117, 118], Drummond [71, 72] and Anco and The [43]. The idea that symmetries exist in pairs, only one member of which is associated with a non-trivial conserved quantity, appears to hold with generality, as we will see in what follows.

4.3.2 Conformal symmetry transformations and Bessel-Hagen’s conservation laws

In the context of electrodynamics, Bessel-Hagen was the first to apply Noether’s theorem [106]. He considered the fifteen parameter group of conformal symmetry transformations and, equipped with the standard Lagrangian density \mathcal{L}_0 , obtained their associated conservation laws. We now consider these symmetry transformations and, as a check on our present approach, confirm that \mathcal{L} leads us to the same conservation laws obtained by Bessel-Hagen.

An infinitesimal conformal symmetry transformation takes the form [119, 120]

$$\begin{aligned} F^{\alpha\beta} \rightarrow F'^{\alpha\beta} &= F^{\alpha\beta} - \partial^\alpha X^\gamma F_\gamma^\beta - \partial^\beta X^\gamma F_\gamma^\alpha - X^\gamma \partial_\gamma F^{\alpha\beta} \\ G^{\alpha\beta} \rightarrow G'^{\alpha\beta} &= G^{\alpha\beta} - \partial^\alpha X^\gamma G_\gamma^\beta - \partial^\beta X^\gamma G_\gamma^\alpha - X^\gamma \partial_\gamma G^{\alpha\beta} \end{aligned} \quad (4.31)$$

with

$$X^\alpha = t^\alpha + w^\alpha_\beta x^\beta + \vartheta x^\alpha + \left(2x^\alpha x^\beta - x_\gamma x^\gamma \eta^{\alpha\beta} \right) a_\beta. \quad (4.32)$$

The components of the infinitesimal four vector t^α and tensor $w^{\alpha\beta} = -w^{\beta\alpha}$ define infinitesimal translations and rotations in spacetime which constitute the Poincaré group [14, 108]. The infinitesimal Lorentz scalar ϑ and the components of the infinitesimal four vector a^α define infinitesimal scale and special conformal transformations, due to Bateman [42, 121] and Cunningham [122]. The physical significance of such transformations is, it seems, not entirely understood: see the work of Rohrlich [108, 123–125], for example. Their independence from the transformations of the Poincaré group has been questioned by Fushchich and Nikitin [117]. Plybon has claimed that the fifteen distinct conformal symmetry transformations are the *only* ones that assume the form seen in (4.31), referred

to by him as being ‘geometric’ [126]. Invoking (4.31) as

$$\begin{aligned} A^\alpha \rightarrow A'^\alpha &= A^\alpha - A_\beta \partial^\alpha X^\beta - X^\beta \partial_\beta A^\alpha + \partial^\alpha (X^\beta A_\beta) \\ C^\alpha \rightarrow C'^\alpha &= C^\alpha - C_\beta \partial^\alpha X^\beta - X^\beta \partial_\beta C^\alpha + \partial^\alpha (X^\beta C_\beta), \end{aligned} \quad (4.33)$$

we obtain, from Noether’s theorem (4.16), the continuity equations

$$\partial_\beta T^{\alpha\beta} = 0 \quad \text{with} \quad T^{\alpha\beta} = \frac{1}{2} (F^\alpha_\gamma F^{\gamma\beta} + G^\alpha_\gamma G^{\gamma\beta}), \quad (4.34)$$

$$\partial_\gamma M^{\alpha\beta\gamma} = 0 \quad \text{with} \quad M^{\alpha\beta\gamma} = x^\alpha T^{\beta\gamma} - x^\beta T^{\alpha\gamma}, \quad (4.35)$$

$$\partial_\alpha D^\alpha = 0 \quad \text{with} \quad D^\alpha = x_\beta T^{\beta\alpha}, \quad (4.36)$$

$$\partial_\beta I^{\alpha\beta} = 0 \quad \text{with} \quad I^{\alpha\beta} = 2x^\alpha x^\gamma T^\beta_\gamma - x_\gamma x^\gamma T^{\alpha\beta}, \quad (4.37)$$

corresponding to translations, rotations and boosts, scale transformations and special conformal transformations [127]. These results (4.34)-(4.37) are essentially the ones advocated by Bessel-Hagen [106], as desired. As is well known, the continuity equation seen in (4.34) embodies the conservation of energy and linear momentum and the continuity equation seen in (4.35) embodies the conservation of rotation angular momentum and boost angular momentum. Of the remaining continuity equations, seen in (4.36) and (4.37), Bessel-Hagen commented that “*the future will show if they have any physical significance*” [106, 128].

We already identified the continuity equation (4.36) heuristically in §3.6.2 (see (3.96)) and recognised there that it embodies the conservation of boost orbital helicity, which, for a single plane wave at least, can be regarded as a statement of the dispersion relation $\omega = |\mathbf{k}|$. This relation connects a time interval (the period of the wave) with a space interval (the wavelength of the wave). This is somewhat appropriate given that the invariance of Maxwell’s equations as written in the strict absence of charge (4.11) and (4.12) under a scale transformation (which, importantly, invokes a dilation or contraction of temporal and spatial properties of the light in equal measure) is itself a reflection of the fact that all periods and wavelengths of light are equally welcome, provided, of course, that they are related such that $\omega = |\mathbf{k}|$. As was noted by Fulton, Rohrlich and Witten [108, 123], by Plybon [120] and, more recently, by Ibragimov [128], the physical significance of the continuity equation (4.37) is, it seems, still not understood. The independence of the continuity equation (4.37) from the others (4.34)-(4.36) has been questioned by Plybon [120].

The infinitesimal conformal symmetry transformation (4.31) possesses a (non-geometric) partner:

$$\begin{aligned} F^{\alpha\beta} \rightarrow F'^{\alpha\beta} &= F^{\alpha\beta} - \partial^\alpha Y^\gamma G^\beta_\gamma - \partial^\beta Y^\gamma G^\alpha_\gamma - Y^\gamma \partial_\gamma G^{\alpha\beta} \\ G^{\alpha\beta} \rightarrow G'^{\alpha\beta} &= G^{\alpha\beta} + \partial^\alpha Y^\gamma F^\beta_\gamma + \partial^\beta Y^\gamma F^\alpha_\gamma + Y^\gamma \partial_\gamma F^{\alpha\beta} \end{aligned} \quad (4.38)$$

for

$$Y^\alpha = g^\alpha + q^\alpha_\beta x^\beta + \psi x^\alpha + (2x^\alpha x^\beta - x_\gamma x^\gamma \eta^{\alpha\beta}) b_\beta, \quad (4.39)$$

with the components of the pseudotensors g^α , $q^{\alpha\beta} = -q^{\beta\alpha}$, ψ and b^α infinitesimal. This (4.38) has also been recognised by Krivskii and Simulik [129, 130] as well as Anco and The [43]. From Noether's theorem (4.16), we find that (4.38) is associated with the conservation of trivial quantities, as noted by Anco and The [43].

4.3.3 The symmetry transformation associated with the conservation of the zilch

Consider now the infinitesimal symmetry transformation

$$\begin{aligned} F^{\alpha\beta} \rightarrow F'^{\alpha\beta} &= F^{\alpha\beta} + \zeta^{\gamma\delta} \partial_\gamma \partial_\delta G^{\alpha\beta} \\ G^{\alpha\beta} \rightarrow G'^{\alpha\beta} &= G^{\alpha\beta} - \zeta^{\gamma\delta} \partial_\gamma \partial_\delta F^{\alpha\beta} \end{aligned} \quad (4.40)$$

with the components of the pseudotensor $\zeta^{\alpha\beta} = \zeta^{\beta\alpha}$ infinitesimal. This (4.40) *resembles* an infinitesimal Heaviside-Larmor rotation (4.25), but differs crucially through the appearance of second derivatives and is not obviously a rotation itself. Invoking (4.40) as

$$\begin{aligned} A^\alpha \rightarrow A'^\alpha &= A^\alpha + \zeta^{\beta\gamma} \partial_\beta \partial_\gamma C^\alpha - \zeta^{\beta\gamma} \partial^\alpha \partial_\beta C_\gamma \\ C^\alpha \rightarrow C'^\alpha &= C^\alpha - \zeta^{\beta\gamma} \partial_\beta \partial_\gamma A^\alpha + \zeta^{\beta\gamma} \partial^\alpha \partial_\beta A_\gamma, \end{aligned} \quad (4.41)$$

we obtain, from Noether's theorem (4.16), the continuity equation

$$\partial_\gamma Z^{\alpha\beta\gamma} = 0 \quad \text{with} \quad Z^{\alpha\beta\gamma} = \frac{1}{2} \left(G^{\gamma\delta} \partial^\alpha F_\delta{}^\beta - F^{\gamma\delta} \partial^\alpha G_\delta{}^\beta \right), \quad (4.42)$$

which embodies the conservation of the zilch, $Z^{\alpha\beta\gamma}$ here being the form of Lipkin's zilch pseudotensor recognised by Morgan [91] and Kibble [93]. The symmetry transformations associated with the individual zilches have been identified variously by Calkin [70] and Przanowski, Rajca and Tosiek [77]. Frequent incorrect identifications of the symmetry transformation associated with the conservation of the zilch [128–131] can be traced to the use of 'Lagrangians' that do not have the dimensions of an energy. Subsequent to publishing the research described in the present chapter [107], the symmetry transformation associated with the conservation of the zilch was also identified and examined by Philbin [132], as well as Lashkari-Ghouchani and Alizadeh [133].

The infinitesimal symmetry transformation (4.40) with which the conservation of zilch is associated possesses a partner:

$$\begin{aligned} F^{\alpha\beta} \rightarrow F'^{\alpha\beta} &= F^{\alpha\beta} + \xi^{\gamma\delta} \partial_\gamma \partial_\delta F^{\alpha\beta} \\ G^{\alpha\beta} \rightarrow G'^{\alpha\beta} &= G^{\alpha\beta} + \xi^{\gamma\delta} \partial_\gamma \partial_\delta G^{\alpha\beta}, \end{aligned} \quad (4.43)$$

with the components of the tensor $\zeta^{\alpha\beta} = \zeta^{\beta\alpha}$ infinitesimal. From Noether's theorem (4.16), we find that (4.43) is associated with the conservation of a trivial quantity that has also emerged in the work of Fradkin [134].

4.3.4 Some simple generalisations

We now demonstrate that there exists an *infinite* number of local symmetry transformations and associated conservation laws.

In §4.3.1-§4.3.3, we saw that the infinitesimal symmetry transformations

$$\delta F^{\alpha\beta} = \theta G^{\alpha\beta} \quad \delta G^{\alpha\beta} = -\theta F^{\alpha\beta}, \quad (4.44)$$

$$\delta F^{\alpha\beta} = g^\gamma \partial_\gamma G^{\alpha\beta} \quad \delta G^{\alpha\beta} = -g^\gamma \partial_\gamma F^{\alpha\beta}, \quad (4.45)$$

$$\delta F^{\alpha\beta} = \zeta^{\gamma\delta} \partial_\gamma \partial_\delta G^{\alpha\beta} \quad \delta G^{\alpha\beta} = -\zeta^{\gamma\delta} \partial_\gamma \partial_\delta F^{\alpha\beta} \quad (4.46)$$

are associated with continuity equations centred upon a helicity four pseudovector h^α (of rank *one*; see (4.27)), a trivial pseudotensor (of rank *two*) and a zilch pseudotensor $Z^{\alpha\beta\gamma}$ (of rank *three*; see (4.42)). In addition, we observed a complimentary structure in that the infinitesimal symmetry transformations

$$\delta F^{\alpha\beta} = \phi F^{\alpha\beta} \quad \delta G^{\alpha\beta} = \phi G^{\alpha\beta}, \quad (4.47)$$

$$\delta F^{\alpha\beta} = t^\gamma \partial_\gamma F^{\alpha\beta} \quad \delta G^{\alpha\beta} = t^\gamma \partial_\gamma G^{\alpha\beta}, \quad (4.48)$$

$$\delta F^{\alpha\beta} = \xi^{\gamma\delta} \partial_\gamma \partial_\delta F^{\alpha\beta} \quad \delta G^{\alpha\beta} = \xi^{\gamma\delta} \partial_\gamma \partial_\delta G^{\alpha\beta} \quad (4.49)$$

are associated with continuity equations centred upon a boost helicity four vector d^α (of rank-*one*; see (4.30)) which is trivial, an energy-momentum tensor $T^{\alpha\beta}$ (of rank-*two*; see (4.34)) and a trivial tensor (of rank-*three*).

These observations are readily generalised:

$$\delta F^{\alpha\beta} = \theta^{\gamma\delta\ldots\omega} \partial_\gamma \partial_\delta \ldots \partial_\omega G^{\alpha\beta} \quad \delta G^{\alpha\beta} = -\theta^{\gamma\delta\ldots\omega} \partial_\gamma \partial_\delta \ldots \partial_\omega F^{\alpha\beta}, \quad (4.50)$$

with the components of the pseudotensor $\theta^{\alpha\beta\ldots\chi}$ infinitesimal, is an infinitesimal symmetry transformation for *any* number of derivatives. It (4.50) is the generalisation of the infinitesimal symmetry transformations seen in (4.44)-(4.46). For one or more derivatives, we find, from Noether's theorem (4.16), that we can associate (4.50) with the continuity equation

$$\partial_\psi H^{\alpha\beta\ldots\chi\psi} = 0 \quad \text{with} \quad H^{\alpha\beta\ldots\chi\psi} = \frac{1}{2} \left(G^{\psi\omega} \partial^\beta \ldots \partial^\chi F_\omega^\alpha - F^{\psi\omega} \partial^\beta \ldots \partial^\chi G_\omega^\alpha \right). \quad (4.51)$$

The existence of this infinite hierarchy of continuity equations centred upon pseudotensors of ever-increasing rank was observed by Morgan [91] (although the helicity continuity equation (4.27) centred upon h^α , which lies 'lowest' amongst these, escaped Morgan's attention). We have now tied them to their associated infinitesimal symmetry transformations (4.50).

In a similar vein,

$$\delta F^{\alpha\beta} = \tau^{\gamma\delta\ldots\omega} \partial_\gamma \partial_\delta \ldots \partial_\omega F^{\alpha\beta} \quad \delta G^{\alpha\beta} = \tau^{\gamma\delta\ldots\omega} \partial_\gamma \partial_\delta \ldots \partial_\omega G^{\alpha\beta}, \quad (4.52)$$

with the components of the tensor $\tau^{\alpha\beta\dots\chi}$ infinitesimal, is an infinitesimal symmetry transformation for any number of derivatives. It (4.52) is the generalisation of the infinitesimal symmetry transformations seen in (4.47)-(4.49). For one or more derivatives, we find, from Noether's theorem (4.16), that we can associate (4.52) with the continuity equation

$$\partial_\psi W^{\alpha\beta\dots\chi\psi} = 0, \quad \text{with} \quad W^{\alpha\beta\dots\chi\psi} = \frac{1}{2} \left(F^{\psi\omega} \partial^\beta \dots \partial^\chi F_\omega^\alpha + G^{\psi\omega} \partial^\beta \dots \partial^\chi G_\omega^\alpha \right). \quad (4.53)$$

The existence of this infinite hierarchy of continuity equations centred upon tensors of ever-increasing rank was also observed by Morgan [91] (although the existence of the boost helicity continuity equation (4.30) centred upon d^α , which lies 'lowest' amongst these tensors, also escaped Morgan's attention). We have now tied them to their associated infinitesimal symmetry transformations (4.52).

The pseudotensors $H^{\alpha\beta\dots\chi\psi}$ of even rank and tensors $W^{\alpha\beta\dots\chi\psi}$ of odd rank describe trivial quantities. The pseudotensors $H^{\alpha\beta\dots\chi\psi}$ of odd rank and the tensors $W^{\alpha\beta\dots\chi\psi}$ of even rank describe non-trivial quantities, the former being dependent upon the *difference* of photon numbers of opposite circular polarisation whereas the latter are dependent upon the *sum*. Thus, we identify a kind of 'alternation' as we ascend rank. This pattern, the first three 'layers' of which we recognise as being the helicity \mathcal{H} , the energy-momentum four-vector \mathcal{T}^α and the zilch $\mathcal{Z}^{\alpha\beta}$;

$$\mathcal{H} = \int \int \int_{-\infty}^{\infty} h^0 d^3\mathbf{r} = \int \int \int_{-\infty}^{\infty} \hbar [n_+(\mathbf{k}) - n_-(\mathbf{k})] d^3\mathbf{k}, \quad (4.54)$$

$$\mathcal{T}^\alpha = \int \int \int_{-\infty}^{\infty} T^{\alpha 0} d^3\mathbf{r} = \int \int \int_{-\infty}^{\infty} \hbar k^\alpha [n_+(\mathbf{k}) + n_-(\mathbf{k})] d^3\mathbf{k}, \quad (4.55)$$

$$\mathcal{Z}^{\alpha\beta} = \int \int \int_{-\infty}^{\infty} Z^{\alpha\beta 0} d^3\mathbf{r} = \int \int \int_{-\infty}^{\infty} \hbar k^\alpha k^\beta [n_+(\mathbf{k}) - n_-(\mathbf{k})] d^3\mathbf{k}, \quad (4.56)$$

appears to extend indefinitely and is, in fact, the pattern the existence of which was conjectured by Candlin [69]. Here, $n_+(\mathbf{k}) = |\tilde{\mathbf{e}}_{\mathbf{k}+} \cdot \tilde{\boldsymbol{\alpha}}(\mathbf{k}, t)|^2 / \hbar$ and $n_-(\mathbf{k}) = |\tilde{\mathbf{e}}_{\mathbf{k}-} \cdot \tilde{\boldsymbol{\alpha}}(\mathbf{k}, t)|^2 / \hbar$ are the classical limits of the photon numbers of the left- and right-handed circular polarisations associated with the wavevector \mathbf{k} [11]. The pieces of this pattern that are dependent upon the difference in photon numbers of opposite circular polarisation in particular have been examined in the quantum domain by Coles and Andrews [135].

The simple picture that we have just painted is enlivened by the existence of an infinite number of continuity equations centred upon tensors and pseudotensors that depend explicitly upon time t and position \mathbf{r} . Consider, for example, those seen in (4.35)-(4.37) which involve the energy-momentum tensor $T^{\alpha\beta}$ and the position four vector x^α . Conserved pseudotensors can also be constructed from the zilch tensor $Z^{\alpha\beta\gamma}$ and x^α , a fact that has been observed by Krivskii and Simulik [129]. In general, such quantities are obscure and we will not consider them further here.

4.3.5 A comment on interpretation

Amongst the continuity equations identified in §4.3.1-§4.3.4, which are infinite in number, there are but a small handful, of low rank, that embody the conservation of quantities with familiar dimensions. In particular, we can readily appreciate the physical significance of helicity, energy, linear momentum, rotation angular momentum and boost angular momentum. We should also comment, however, on those higher-order continuity equations, including most of those seen in (4.51) and (4.53), that embody the conservation of quantities with unfamiliar dimensions. It seems that the existence of these reflects the *self similarity* inherent in Maxwell's equations as written in the strict absence of charge (4.11) and (4.12) which was discussed in §2.2. Specifically, we suggest that these higher-order conserved quantities describe properties of various *derivatives* of \mathbf{E} and \mathbf{B} , in the manner that we elucidated in §3.4 for the zilch in particular.

4.4 Non-local symmetry transformations and their associated conservation laws

We turn our attention now to non-local symmetry transformations, in which the changes $\delta\mathbf{E}$ and $\delta\mathbf{B}$ in the electric field \mathbf{E} and the magnetic flux density \mathbf{B} do *not* depend exclusively upon the latter and perhaps their various derivatives at the same time t and position \mathbf{r} . In considering these symmetry transformations, the language of tensor and pseudotensor calculus fails us and we therefore revert directly to the canonical forms of their associated local continuity equations, which are to be understood in what follows.

4.4.1 van Enk-Nienhuis-Barnett rotations and the conservation of spin, Barnett rotations and the conservation of orbital angular momentum

An infinitesimal rotation of the light about the origin $\mathbf{r} = 0$ takes the form

$$\begin{aligned}\mathbf{E} &\rightarrow \mathbf{E}' = \mathbf{E} + \boldsymbol{\theta} \times \mathbf{E} - \boldsymbol{\theta} \cdot (\mathbf{r} \times \nabla) \mathbf{E} \\ \mathbf{B} &\rightarrow \mathbf{B}' = \mathbf{B} + \boldsymbol{\theta} \times \mathbf{B} - \boldsymbol{\theta} \cdot (\mathbf{r} \times \nabla) \mathbf{B},\end{aligned}\tag{4.57}$$

with $\boldsymbol{\theta}$ an infinitesimal time-even pseudovector, the magnitude and orientation of which define the angle and sense of the rotation. The first contribution seen in (4.57) rotates the orientations of the electric field vectors and magnetic flux density pseudovectors whilst the second contribution rotates the spatial distribution of the light. This is a *local* infinitesimal symmetry transformation and constitutes part of the infinitesimal conformal symmetry transformation seen in (4.31), with $w^{23} = -w^{32} = \theta_x$, $w^{31} = -w^{13} = \theta_y$ and $w^{12} = -w^{21} = \theta_z$. The x , y and z components of the associated global conservation law

$$\mathcal{J} = \iiint_{\infty} \mathbf{r} \times (\mathbf{E} \times \mathbf{B}) \, d^3\mathbf{r} = \text{constant}$$

for the rotation angular momentum \mathcal{J} , seen also in (3.15), follow from the continuity equation seen in (4.35) for $\alpha\beta = 23, 31$ and 12 , say. As was discussed in §3.2, \mathcal{J} is itself the sum of separately

conserved spin \mathcal{S} and orbital \mathcal{L} pieces. It should be possible, therefore, to separate (4.57) into pieces separately associated with the conservation of spin and with the conservation of orbital angular momentum. At first glance, it is natural, perhaps, to suggest that

$$\begin{aligned}\mathbf{E} &\rightarrow \mathbf{E}' = \mathbf{E} + (\boldsymbol{\theta} \times \mathbf{E}) \\ \mathbf{B} &\rightarrow \mathbf{B}' = \mathbf{B} + (\boldsymbol{\theta} \times \mathbf{B})\end{aligned}\tag{4.58}$$

is associated with the conservation of spin and

$$\begin{aligned}\mathbf{E} &\rightarrow \mathbf{E}' = \mathbf{E} - \boldsymbol{\theta} \cdot (\mathbf{r} \times \nabla) \mathbf{E} \\ \mathbf{B} &\rightarrow \mathbf{B}' = \mathbf{B} - \boldsymbol{\theta} \cdot (\mathbf{r} \times \nabla) \mathbf{B}\end{aligned}\tag{4.59}$$

is associated with the conservation of orbital angular momentum. Neither (4.58) nor (4.59) is by itself an acceptable transformation, however. In particular, neither respect the solenoidal character of \mathbf{E} and \mathbf{B} ($\nabla \cdot \mathbf{E}' \neq 0$, $\nabla \cdot \mathbf{B}' \neq 0$) and thus are not symmetry transformations, an observation made explicitly by Barnett [44]. Such incorrect associations have led some to claim, erroneously, that the spin and orbital angular momentum of light are not separately meaningful [11]. The situation was clarified by the work of van Enk and Nienhuis [59, 60] and Barnett [44], however, who established that the operators $\hat{\mathcal{S}}$ and $\hat{\mathcal{L}}$ representing \mathcal{S} and \mathcal{L} *do* generate symmetry transformations which differ, of course, from the assumed forms seen in (4.58) and (4.59). Following their work, we observe that (4.57) can be expressed *equivalently*⁴ as

$$\begin{aligned}\mathbf{E} &\rightarrow \mathbf{E}' = \mathbf{E} + (\boldsymbol{\theta} \times \mathbf{E})^\perp - [\boldsymbol{\theta} \cdot (\mathbf{r} \times \nabla) \mathbf{E}]^\perp \\ \mathbf{B} &\rightarrow \mathbf{B}' = \mathbf{B} + (\boldsymbol{\theta} \times \mathbf{B})^\perp - [\boldsymbol{\theta} \cdot (\mathbf{r} \times \nabla) \mathbf{B}]^\perp.\end{aligned}\tag{4.60}$$

The first contribution

$$\begin{aligned}\mathbf{E} &\rightarrow \mathbf{E}' = \mathbf{E} + (\boldsymbol{\theta} \times \mathbf{E})^\perp \\ \mathbf{B} &\rightarrow \mathbf{B}' = \mathbf{B} + (\boldsymbol{\theta} \times \mathbf{B})^\perp\end{aligned}\tag{4.61}$$

seen in (4.60) is the closest approximation to an infinitesimal rotation of the orientations of the electric field vectors and magnetic flux density pseudovectors, in the sense defined by $\boldsymbol{\theta}$, that is consistent with the requirement that the transformed electric field \mathbf{E}' and the transformed magnetic flux density \mathbf{B}' be solenoidal. This (4.61) is a *non-local* infinitesimal symmetry transformation which sees the electric field vectors and magnetic flux density pseudovectors of each plane wave comprising the light rotated about its wavevector \mathbf{k} through an angle $\theta_{(a)} \hat{k}_{(a)}$. We refer to (4.61) as an infinitesimal van Enk-Nienhuis-Barnett rotation. Employing Noether's theorem (4.16) we find, following some manipulations, that

$$\dot{s}_{(a)} + \partial_b n_{(ab)} = 0,$$

⁴Note that $(\boldsymbol{\theta} \times \mathbf{E})^\parallel - [\boldsymbol{\theta} \cdot (\mathbf{r} \times \nabla) \mathbf{E}]^\parallel = (\boldsymbol{\theta} \times \mathbf{B})^\parallel - [\boldsymbol{\theta} \cdot (\mathbf{r} \times \nabla) \mathbf{B}]^\parallel = 0$.

which embodies the conservation of spin, being the spin continuity equation (3.45) which we originally identified heuristically. The second contribution

$$\begin{aligned}\mathbf{E} &\rightarrow \mathbf{E}' = \mathbf{E} - [\boldsymbol{\theta} \cdot (\mathbf{r} \times \nabla) \mathbf{E}]^\perp \\ \mathbf{B} &\rightarrow \mathbf{B}' = \mathbf{B} - [\boldsymbol{\theta} \cdot (\mathbf{r} \times \nabla) \mathbf{B}]^\perp,\end{aligned}\quad (4.62)$$

seen in (4.60) is the closest approximation to an infinitesimal rotation of the spatial distribution of the light, in the sense defined by $\boldsymbol{\theta}$, that is consistent with the requirement that \mathbf{E}' and \mathbf{B}' be solenoidal. This is also a *non-local* infinitesimal symmetry transformation. We refer to (4.62) as an infinitesimal Barnett rotation. Employing Noether's theorem (4.16) we find, following some manipulations, that (4.62) is associated with the continuity equation

$$\dot{l}_{(a)} + \partial_b o_{(ab)} = 0,$$

which embodies the conservation of orbital angular momentum, being the orbital angular momentum continuity equation (3.81) which we originally identified heuristically and which has been reported recently elsewhere by Bliokh, Dressel and Nori [101].

4.4.2 Generalised Heaviside-Larmor rotations and the conservation of the *ab* infra zilches

In §4.3.1, we demonstrated that Heaviside-Larmor rotations are associated with the conservation of helicity ($\pm\hbar$ per circularly polarised plane-wave-mode photon of wavevector \mathbf{k} and polarisation parameter $\sigma = \pm 1$). In §4.4.1, we demonstrated that van Enk-Nienhuis-Barnett rotations are associated with the conservation of spin (components $\pm\hbar\hat{k}_{(a)}$ per photon). As was discussed in §3.3, helicity and spin are, however, but the first two members of an *infinite* collection of intrinsic rotation angular momenta. We now turn our attention explicitly to the next member after spin, namely the *ab* infra zilches ($\pm\hbar\hat{k}_{(a)}\hat{k}_{(b)}$ per photon).

We observe here that

$$\begin{aligned}E_{(a)} &\rightarrow E'_{(a)} = E_{(a)} + \theta_{(bb)}B_{(a)} - [\theta_{(ab)}B_{(b)}]^\perp - \epsilon_{(abc)}\partial_b \left[\theta_{(cd)}A_{(d)}^\perp \right]^\perp \\ B_{(a)} &\rightarrow B'_{(a)} = B_{(a)} - \theta_{(bb)}E_{(a)} + [\theta_{(ab)}E_{(b)}]^\perp - \epsilon_{(abc)}\partial_b \left[\theta_{(cd)}C_{(d)}^\perp \right]^\perp,\end{aligned}\quad (4.63)$$

with $\theta_{(ab)} = \theta_{(ba)}$ a rotational pseudotensor of infinitesimal angles, is a non-local infinitesimal symmetry transformation which sees the electric field vectors and magnetic flux density pseudovectors of each plane wave comprising the light rotated about its wavevector \mathbf{k} through an angle $\theta_{(ab)}\hat{k}_{(a)}\hat{k}_{(b)}$. We refer to (4.63) as an infinitesimal generalised Heaviside-Larmor rotation. Employing Noether's theorem (4.16) we find, following some manipulations, that (4.63) is associated with the continuity equation

$$\dot{n}_{(ab)} + \partial_c N^{abc} = 0$$

which embodies the local and hence global conservation of the ab infra zilches, being the ab infra zilch continuity equation (3.46) which we originally identified heuristically.

In light of the results presented in §4.3.1, §4.4.1 and above, we now infer the non-local infinitesimal symmetry transformations underlying the conservation of the remaining members of the infinite collection of intrinsic rotation angular momenta discussed in §3.3: the conservation of the three-component quantity $(\pm \hbar \hat{k}_{(a)} \hat{k}_{(b)} \hat{k}_{(c)})$ per photon) for example, is associated with a rotation of each plane wave comprising the light about its wavevector \mathbf{k} through an infinitesimal angle $\theta_{(abc)} \hat{k}_{(a)} \hat{k}_{(b)} \hat{k}_{(c)}$, and so on, ad infinitum.

4.4.3 The symmetry transformations associated with the conservation of boost spin and the conservation of boost orbital angular momentum

An infinitesimal boost of the light ‘about’ time $t = 0$ and $\mathbf{r} = 0$ takes the form

$$\begin{aligned} \mathbf{E} \rightarrow \mathbf{E}' &= \mathbf{E} - \boldsymbol{\phi} \times \mathbf{B} - \boldsymbol{\phi} \cdot \left(t \boldsymbol{\nabla} + \mathbf{r} \frac{\partial}{\partial t} \right) \mathbf{E} \\ \mathbf{B} \rightarrow \mathbf{B}' &= \mathbf{B} + \boldsymbol{\phi} \times \mathbf{E} - \boldsymbol{\phi} \cdot \left(t \boldsymbol{\nabla} + \mathbf{r} \frac{\partial}{\partial t} \right) \mathbf{B}, \end{aligned} \quad (4.64)$$

with $\boldsymbol{\phi}$ an infinitesimal time-odd vector, the magnitude and orientation of which define the rapidity and direction of the boost. The first contribution seen in (4.64) mixes the electric field vectors and magnetic flux density pseudovectors whilst the second contribution rotates the spacetime distribution of the light in a hyperbolic manner. This is a *local* symmetry transformation and constitutes part of the infinitesimal conformal symmetry transformation seen in (4.31), with $w^{10} = -w^{01} = \phi_x$, $w^{20} = -w^{02} = \phi_y$ and $w^{30} = -w^{03} = \phi_z$. The x, y and z components of the associated global conservation law

$$\mathcal{K} = \iiint_{\infty} \left[t \mathbf{E} \times \mathbf{B} - \frac{1}{2} \mathbf{r} (\mathbf{E} \cdot \mathbf{E} + \mathbf{B} \cdot \mathbf{B}) \right] d^3 \mathbf{r} = \text{constant}$$

for the boost angular momentum \mathcal{K} , seen also in (3.19), follow from the continuity equation seen in (4.35), with $\alpha\beta = 01, 02$ and 03 , say. As was described in §3.2, an attempt was made recently by Barnett to separate \mathcal{K} into boost spin \mathcal{V} and boost orbital \mathcal{Y} parts [45]. We now pursue this idea in the context of Noether’s theorem.

Working by analogy with the approach taken in §4.4.1 for spin and orbital angular momentum, we observe here that (4.64) can be expressed equivalently as

$$\begin{aligned} \mathbf{E} \rightarrow \mathbf{E}' &= \mathbf{E} - (\boldsymbol{\phi} \times \mathbf{B})^\perp - \left[\boldsymbol{\phi} \cdot \left(t \boldsymbol{\nabla} + \mathbf{r} \frac{\partial}{\partial t} \right) \mathbf{E} \right]^\perp \\ \mathbf{B} \rightarrow \mathbf{B}' &= \mathbf{B} + (\boldsymbol{\phi} \times \mathbf{E})^\perp - \left[\boldsymbol{\phi} \cdot \left(t \boldsymbol{\nabla} + \mathbf{r} \frac{\partial}{\partial t} \right) \mathbf{B} \right]^\perp. \end{aligned} \quad (4.65)$$

The first contribution

$$\begin{aligned}\mathbf{E} \rightarrow \mathbf{E}' &= \mathbf{E} - (\boldsymbol{\phi} \times \mathbf{B})^\perp \\ \mathbf{B} \rightarrow \mathbf{B}' &= \mathbf{B} + (\boldsymbol{\phi} \times \mathbf{E})^\perp\end{aligned}\tag{4.66}$$

seen in (4.65) is the closest approximation to an infinitesimal mixing of the electric field vectors and magnetic flux density pseudovectors, in the sense defined by $\boldsymbol{\phi}$, that is consistent with the requirement that \mathbf{E}' and \mathbf{B}' be solenoidal. This is a *non-local* infinitesimal symmetry transformation which sees the electric field vectors and magnetic flux density pseudovectors of each plane wave comprising the light boosted in the direction of its wavevector \mathbf{k} through a rapidity $\phi_{(a)} \hat{k}_{(a)}$. Employing Noether's theorem (4.16) we find, following some manipulations, that (4.66) is associated with the continuity equation

$$\dot{v}_{(a)} + \partial_b q_{(ab)} = 0$$

which embodies the conservation of boost spin, being the boost spin continuity equation (3.89) which we originally identified heuristically. The second contribution

$$\begin{aligned}\mathbf{E} \rightarrow \mathbf{E}' &= \mathbf{E} - \left[\boldsymbol{\phi} \cdot \left(t \boldsymbol{\nabla} + \mathbf{r} \frac{\partial}{\partial t} \right) \mathbf{E} \right]^\perp \\ \mathbf{B} \rightarrow \mathbf{B}' &= \mathbf{B} - \left[\boldsymbol{\phi} \cdot \left(t \boldsymbol{\nabla} + \mathbf{r} \frac{\partial}{\partial t} \right) \mathbf{B} \right]^\perp,\end{aligned}\tag{4.67}$$

seen in (4.60) is the closest approximation to an infinitesimal hyperbolic rotation of the spacetime distribution of the light, in the sense defined by $\boldsymbol{\phi}$, that is consistent with the requirement that \mathbf{E}' and \mathbf{B}' be solenoidal. Employing Noether's theorem (4.16) we find, following some manipulations, that (4.67) is associated with the continuity equation

$$\dot{y}_{(a)} + \partial_b f_{(ab)} = 0,$$

which embodies the conservation of boost orbital angular momentum, being the boost orbital angular momentum continuity equation (3.93) which we originally identified heuristically. The effects of (4.66) and (4.67) on a single linearly polarised plane wave are depicted in figures 4.3 and 4.4.

It will be noticed that the infinitesimal boost spin symmetry transformation (4.66) is the partner of the infinitesimal spin symmetry transformation (4.61). The vanishing of \mathfrak{V} thus falls in line with our general observations regarding such symmetry pairs. Following the results presented in §4.3.1 and above, the symmetry transformations underlying the conservation of the remaining members of the infinite collection of intrinsic boost angular momenta introduced in §3.6.1 may also be readily inferred, being the partners of those underlying the conservation of the infinite collection of intrinsic rotation angular momenta introduced in §3.3: boosting the electric field vectors and magnetic flux density pseudovectors of each plane wave comprising the light in the direction of its wavevector \mathbf{k} through an infinitesimal rapidity $\phi_{(ab)} \hat{k}_{(a)} \hat{k}_{(b)}$ for example, is also an infinitesimal symmetry transformation and is the partner of that underlying the conservation of the ab infra zilches; a pattern that can extend indefinitely. We also note here for completeness that the partners of the infinitesimal

orbital angular momentum symmetry transformation (4.62) and the infinitesimal boost orbital angular momentum symmetry transformation (4.67) are seemingly obscure and are associated, through Noether's theorem (4.16), with the conservation of trivial quantities.

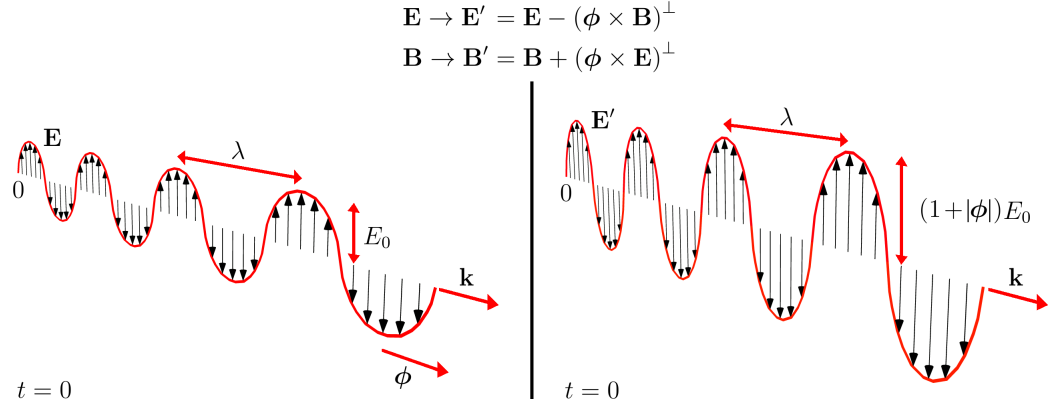


Figure 4.3: The effect of an infinitesimal boost spin symmetry transformation (4.66) on a single linearly polarised plane wave, with the rapidity vector $\boldsymbol{\phi}$ parallel to the wavevector \mathbf{k} of the wave. The amplitude E_0 of the wave is increased to $(1 + |\boldsymbol{\phi}|)E_0$, leaving the spacetime distribution of the wave unchanged. Electric field vectors are depicted by black arrows. Magnetic flux density pseudovectors are omitted, for the sake of clarity.

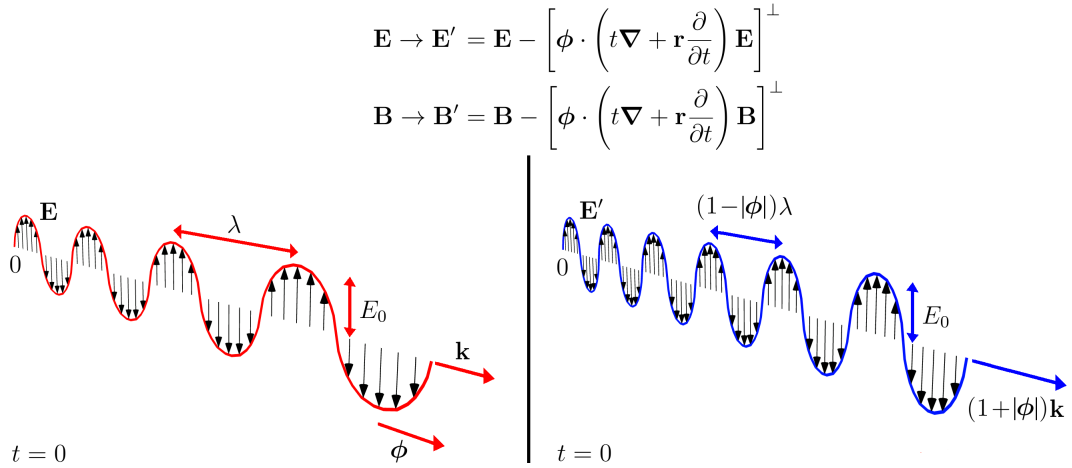


Figure 4.4: The effect of an infinitesimal boost orbital symmetry transformation (4.67) on a single linearly polarised plane wave, with the rapidity vector $\boldsymbol{\phi}$ parallel to the wavevector \mathbf{k} of the wave. The spacetime distribution of the wave is modified such that the wavelength λ of the wave is blue shifted to $(1 - |\boldsymbol{\phi}|)\lambda$, leaving the amplitude E_0 of the wave unchanged. Electric field vectors are depicted by black arrows. Magnetic flux density pseudovectors are omitted, for the sake of clarity.

4.4.4 More non-local symmetry transformations and their associated conservation laws

Owing, it seems, to the self similarity inherent in Maxwell's equations as written in the strict absence of charge (4.11) and (4.12) which was discussed in §2.2, there exists an *infinite* number of non-local symmetry transformations and associated conservation laws. Unlike those considered in §4.4.1-§4.4.3, the majority of these conserved quantities are rather obscure however, possessing unfamiliar dimensions. We suggest that they describe properties of various *integrals* of \mathbf{E} and \mathbf{B} . To illustrate

this, let us consider the infinitesimal symmetry transformation

$$\begin{aligned}\mathbf{E} &\rightarrow \mathbf{E}' = \mathbf{E} + \alpha \mathbf{A}^\perp \\ \mathbf{B} &\rightarrow \mathbf{B}' = \mathbf{B} + \alpha \mathbf{C}^\perp,\end{aligned}\tag{4.68}$$

with the rotational scalar α infinitesimal. Through Noether's theorem (4.16), we find, following some manipulations, that (4.68) is associated with the continuity equation

$$\frac{\partial}{\partial t} \frac{1}{2} \left(\mathbf{A}^\perp \cdot \mathbf{A}^\perp + \mathbf{C}^\perp \cdot \mathbf{C}^\perp \right) + \nabla \cdot \left(\mathbf{A}^\perp \times \mathbf{C}^\perp \right) = 0,\tag{4.69}$$

which embodies the conservation of the 'energy' of the first and second potentials \mathbf{A}^\perp and \mathbf{C}^\perp . Such observations may be readily extended. This particular continuity equation (4.69) has also been recognised by Drummond [71, 72]. Naturally, we find that the partner symmetry of (4.68) is associated with the conservation of a trivial quantity. The existence of various non-local symmetry transformations has also been recognised by Fushchich and Nikitin [117, 118].

4.4.5 On the trivial nature of boost helicity, boost spin etc

In order to elucidate the trivial nature of boost helicity, boost spin etc, let us highlight here, in a general manner, that there is a distinction between the *existence* of a symmetry transformation and its associated conservation law, and the *actual* dynamics exhibited by a system and the value consequently taken by the conserved quantity. Moreover, the dynamics that a system must exhibit to possess a non-vanishing value of a conserved quantity usually reflect the associated symmetry transformation, whilst the sign of this value depends upon whether the motion goes with or against the grain of the symmetry transformation.

To give a tangible example: consider a point particle in the absence of other influences. The symmetry transformation that is a translation of the particle in the $+x$ direction, say, is associated, of course, with the conservation of the x component of the particle's linear momentum. If the particle then happens to move in the same sense as this symmetry transformation (that is, in the $+x$ direction), the x component of the particle's linear momentum is positive whereas if the particle moves in the sense opposite to this symmetry transformation (that is, in the $-x$ direction), the x component of the particle's linear momentum is negative.

We can perhaps understand the trivial nature of boost helicity, boost spin etc in these terms. We focus upon boost helicity. The infinitesimal boost helicity symmetry transformation (4.28) multiplies the amplitude of each (linearly polarised, for the sake of this argument) plane wave comprising the light by a factor of $1 + \phi$, which is emphatically an *increase* in amplitude, for $\phi > 0$ of course. Light is *oscillatory*, however, and as t passes at any given \mathbf{r} , each wave goes with the grain of the infinitesimal boost helicity symmetry transformation (4.66) as often as against it. Associated with these respective motions are positive and negative contributions to the boost helicity \mathcal{D} and the latter thus vanishes, being an integral over all \mathbf{r} that is independent of t . Such arguments also apply, of course, to boost spin etc.

Whilst publishing the research described in the present chapter [107], an anonymous referee pointed out that it is also possible to interpret the vanishing of \mathcal{D} as a statement of the global conservation of the ‘energy’ of \mathbf{A}^\perp and \mathbf{C}^\perp , as

$$\begin{aligned} \frac{d}{dt} \iiint_{\infty} \frac{1}{2} \left(\mathbf{A}^\perp \cdot \mathbf{A}^\perp + \mathbf{C}^\perp \cdot \mathbf{C}^\perp \right) d^3\mathbf{r} &= 2\mathcal{D} \\ &= 0. \end{aligned} \quad (4.70)$$

Similarly, the vanishing of the boost spin \mathcal{V} is a statement of the global conservation of the ‘linear momentum’ of \mathbf{A}^\perp and \mathbf{C}^\perp , as

$$\begin{aligned} \frac{d}{dt} \iiint_{\infty} \mathbf{A}^\perp \times \mathbf{C}^\perp d^3\mathbf{r} &= 2\mathcal{V} \\ &= 0 \end{aligned} \quad (4.71)$$

and so on, ad infinitum.

Arguments of this nature can also be applied more generally, perhaps, to appreciate why only one member of any symmetry transformation pair is associated with the conservation of a non-trivial quantity.

4.5 Discussion

We have introduced a variational description of freely propagating light that is based upon the democratic acknowledgement of both electric and magnetic potentials. We have used this description together with Noether’s theorem to investigate symmetries and their associated conservation laws. Analogous approaches can be pursued in other branches of physics, as was recently demonstrated for weak gravitational waves propagating freely in a flat spacetime background by Barnett [136].

There remains much to be explored, even with regards to the symmetries and their associated conservation laws that we have already considered: what is the physical significance of special conformal transformations and their associated conservation law, for example? I would also like to understand in full our general observation that symmetries exist in pairs, only one member of which is associated with the conservation of a non-trivial quantity. It is possible to utilise the formalism of *general* relativity and examine our results in other coordinate systems, wherein they appear to offer different information: the azimuthal component in cylindrical coordinates of the canonical continuity equation for *linear* momentum is a continuity equation for the z component of *orbital* angular momentum [137], for example.

It is clear in addition that there exist many more symmetries and associated conservation laws than those that we have considered in the present chapter: consider, for example, the conservation of

photon number and the classical limit thereof⁵, which does not appear anywhere in the hierarchies that we have identified. An important question pertains to the independence of symmetries and their associated conservation laws. A group theoretical analysis may be illuminating in this regard. In general, I am interested in the possibility (or lack thereof) of applying Noether's theorem, in some form, to study discrete rather than continuous symmetry transformations⁶: as we have demonstrated in §4.4, the non-locality of a symmetry transformation does not by itself preclude the application of Noether's theorem.

The inclusion of charge constitutes a subtle problem that I wish to investigate, in particular because it may afford a route by which to explore further my belief that electric-magnetic democracy is intimately associated with the quantisation of charge [4–7]. Moreover, the extension of our formalism to the quantum domain and in particular the usual canonical quantisation procedure brings its own challenges, owing, it seems, to the problem of overdetermination.

The above are tasks for future research.

⁵The associated infinitesimal symmetry transformation can be invoked, in fact, at the level of the normal variables $\tilde{\alpha}$ as $\tilde{\alpha} \rightarrow \tilde{\alpha}' = \tilde{\alpha} - i\vartheta\tilde{\alpha}$, which is an infinitesimal phase shift of the light through ϑ .

⁶An obvious approach is to modify a discrete symmetry transformation by multiplying the associated changes $\delta\mathbf{E}$ and $\delta\mathbf{B}$ in the electric field \mathbf{E} and the magnetic flux density \mathbf{B} by an infinitesimal dimensionless quantity. Through Noether's theorem (4.16) we find for example that time and / or parity inversions, when treated in this manner, lead to conservation laws for trivial quantities, however.

Chapter 5

Chirality and Optical Activity

5.1 Introduction

The word ‘chiral’ was introduced by Kelvin to refer to any geometrical figure or group of points that cannot be brought into coincidence with its mirror image, thus possessing a sense of handedness [138, 139]. It derives, in fact, from the Greek word for hand; $\chi\epsilon\iota\rho\alpha$ [140]. In the language of point group theory, a chiral entity is said to be devoid of improper rotational symmetry elements and must, therefore, belong to one of the point groups C_n , D_n , O , T or I , in the Schoenflies notation [12, 25, 27]. Kelvin’s definition of chirality was recently extended by Barron to include *time*, leading him to distinguish between ‘true’ and ‘false’ chirality, the former being exhibited by systems that exist in two distinct enantiomeric states interconvertable, up to circular rotations, by parity inversion but not by time reversal [141, 142]. Chirality pervades the natural world [143]; from the enigmatic preferences of the electroweak interaction [144, 145] to the arms of individual spiral and elliptical galaxies [146]: see figure 5.1.



Figure 5.1: Chirality is ubiquitous. Indeed, all entities that are not achiral are chiral.

Many *molecules* are chiral owing to the nature and arrangement in space of their constituent atoms [143]. The mirror-image forms, or ‘enantiomers’, of a chiral molecule often enjoy separate and seemingly¹ stable existences (see figure 5.2) and are observed to behave identically in many circumstances but differently in others [25, 143]. The fact is well established in particular that molecular

¹The very existence of chiral molecules appears at first glance to be at odds with fundamental ideas from quantum mechanics. This, Hund’s paradox [25], is still the subject of occasional debate.

chirality is crucial to biological function [143, 147], as is reflected strikingly by the existence of chiral molecules the enantiomers of which interact differently with living things: one enantiomer of carvone is found in spearmint leaves whereas the opposite enantiomer is found in caraway seeds, thus being associated with different aromas; one enantiomer of methamphetamine is recognised as being a harmful narcotic whereas the opposite enantiomer is employed as a decongestant; one enantiomer of mecoprop functions as a herbicide whereas the opposite enantiomer is ineffective in this context. The ability to characterise, discriminate between and resolve the enantiomers of a chiral molecule is desirable in both academic and industrial contexts and yet, remains elusive in many cases. Thus, the development of means by which to probe and utilise molecular chirality constitutes a vibrant field of modern research [148, 149].

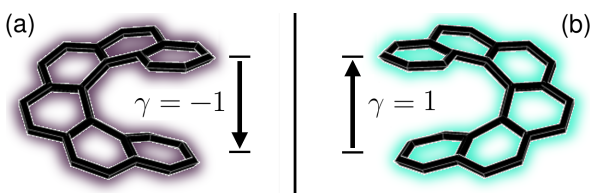


Figure 5.2: The left- (a) and right-handed (b) enantiomers of hexahelicene, a chiral molecule with a shape resembling that of a finite cylindrical helix the synthesis of which was first reported by Newman, Lutz and Lednicer [25, 34, 35]. The normalised pitch γ of hexahelicene is a rotational pseudoscalar, assuming opposite signs for the molecule's opposite enantiomers [25].

Many types of *light* are chiral. Principal amongst these is perhaps circularly polarised light, in which the electric field vectors and magnetic flux density pseudovectors trace out either left- or right-handed cylindrical helices in space, these being prototypical chiral figures, of course. Naturally, a given chiral molecule interacts differently with left- and right-handed circularly polarised light [25, 143], much as a given human hand interacts differently with left- and right-handed gloves. The study and utilisation of these differences is one of the principal means by which we probe and manipulate chiral molecules. We follow Barron and use the phrase ‘optical activity’ in a general manner to refer to light-matter interactions with characteristics attributable to a discrimination, on some level, between left- and right-handed circular polarisations [25]. Chiral molecules are then said to exhibit natural optical activity. The subject that is optical activity and its applications extends somewhat beyond the domain of molecular chirality, however, as optical activity is also exhibited naturally by certain orientated achiral molecules and can be induced, moreover, in all atoms and molecules by static magnetic fields and, in some circumstances, by static electric fields [25].

In the present chapter, we observe that many optical activity phenomena can be related explicitly to helicity, spin, the *ab* infra zilches etc. This is unsurprising, perhaps, given that these angular momenta differ in value for left- and right-handed circularly polarised light. We employ this new insight in the consideration of a well-established manifestation of optical activity (optical rotation; §5.2), a dormant manifestation of optical activity (differential scattering; §5.3) and a new manifestation of optical activity (discriminatory optical force for chiral molecules; §5.4). The text is based primarily upon my research papers [150], [151] and [152].

5.2 Optical rotation

The study of optical activity began, it seems, with the discovery by Arago of a spectrum of colours whilst viewing sunlight that had passed along the optic axis of a quartz crystal placed between polarisers [25, 153]. It was established in subsequent experiments by Biot that these colours are attributable to two distinct effects which we now refer to in general as optical rotation: the rotation of the plane of polarisation of linearly polarised light upon traversing a rotatory medium, and optical rotatory dispersion: the frequency dependence of this rotation [25]. Optical rotation has since been identified in an abundance of contexts and is employed today in a wealth of different applications, from the determination of sugar concentrations to the operation of liquid crystal displays.

Following his discovery of circularly polarised light, Fresnel attributed optical rotation to circular birefringence: a difference in the speeds of propagation supported by a rotatory medium for the left- and right-handed circularly polarised components of linearly polarised light [25]. If $n_+(c|\mathbf{k}_0|)$ and $n_-(c|\mathbf{k}_0|)$ are the phase refractive indices supported at angular frequency $c|\mathbf{k}_0|$ by a rotatory medium for left- and right-handed circular polarisations, the angle $\theta(c|\mathbf{k}_0|)$ of optical rotation suffered by linearly polarised light of angular frequency $c|\mathbf{k}_0|$ upon traversing a geometrical path length l is

$$\theta(c|\mathbf{k}_0|) = \frac{1}{2} [n_+(c|\mathbf{k}_0|) - n_-(c|\mathbf{k}_0|)] |\mathbf{k}_0| l. \quad (5.1)$$

Microscopic theories of optical rotation based upon light scattering can be found in books by Barron [25] and Craig and Thirunamachandran [12].

It is natural, perhaps, to ask if optical rotation can be related to the angular momentum of light. In the present section, we explore this possibility through the introduction of a novel quantum mechanical theory in which optical refraction is attributed to an *interaction energy* shared between light and a medium through which the light propagates. In certain rotatory media, this interaction energy is seen to depend upon the helicity and / or spin of the light which differ in value, of course, for left- and right-handed circular polarisations. These differences give rise in turn to circular birefringence and hence, optical rotation. Our theory is complementary to those discussed above and leads us moreover to identify and explore an entirely new manifestation of optical activity in §5.4.

5.2.1 The model medium

Working in the quantum domain, let us consider a model medium comprised of N_{mol} molecules (or atoms), each of which is itself comprised identically of N_e electrons and N_n nuclei. Following the results presented in §1.3.1, we separate the operator \hat{H} representing the Hamiltonian of the system ‘light + medium’ as

$$\hat{H} = \hat{H}_0 + \hat{V}, \quad (5.2)$$

where the first operator \hat{H}_0 describes the light and the individual molecules *decoupled* whilst the second operator \hat{V} describes the *interaction* between the light and the molecules as well as the Coulomb interactions between the molecules. Under the governance of \hat{H}_0 alone, the light and the

individual molecules would thus evolve independently of one another and it is \hat{V} , therefore, that must give rise to optical refraction and optical rotation. Explicitly we take

$$\hat{H}_0 = \hat{H}_{\text{rad}} + \sum_{\xi=1}^{N_{\text{mol}}} \hat{H}_{\text{mol}\xi}, \quad (5.3)$$

$$\hat{V} = \sum_{\xi=1}^{N_{\text{mol}}} \hat{H}_{\text{int}} + \sum_{\xi=1}^{N_{\text{mol}}-1} \sum_{\xi'=1}^{N_{\text{mol}}} \hat{H}_{\text{Coul}\xi\xi'}, \quad (5.4)$$

with

$$\hat{H}_{\text{rad}} = \iiint_V \frac{1}{2} (\hat{\mathbf{\Pi}}^2 + |\nabla \times \hat{\mathbf{A}}|^2) d^3\mathbf{r}, \quad (5.5)$$

$$\begin{aligned} \hat{H}_{\text{mol}\xi} = & \sum_{i=1}^{N_e} \frac{\hat{\mathbf{p}}_{i\xi}^2}{2m_e} + \sum_{j=1}^{N_n} \frac{\hat{\mathbf{P}}_{j\xi}^2}{2M_j} \\ & + \sum_{i=1}^{N_e-1} \sum_{i'=1}^{N_e} \frac{e^2}{4\pi\epsilon_0 |\hat{\mathbf{r}}_{i\xi} - \hat{\mathbf{r}}_{i'\xi}|} - \sum_{i=1}^{N_e} \sum_{j=1}^{N_n} \frac{Z_j e^2}{4\pi\epsilon_0 |\hat{\mathbf{r}}_{i\xi} - \hat{\mathbf{R}}_{j\xi}|} \\ & + \sum_{j=1}^{N_n-1} \sum_{j'=1}^{N_n} \frac{Z_j Z_{j'} e^2}{4\pi\epsilon_0 |\hat{\mathbf{R}}_{j\xi} - \hat{\mathbf{R}}_{j'\xi}|}, \end{aligned} \quad (5.6)$$

$$\begin{aligned} \hat{H}_{\text{int}\xi} = & \sum_{i=1}^{N_e} \frac{e}{m_e} \hat{\mathbf{p}}_{i\xi} \cdot \hat{\mathbf{A}}(\hat{\mathbf{r}}_{i\xi}) + \sum_{i=1}^{N_e} \frac{e^2}{2m_e} |\hat{\mathbf{A}}(\hat{\mathbf{r}}_{i\xi})|^2 \\ & - \sum_{j=1}^{N_n} \frac{Z_j e}{M_j} \hat{\mathbf{P}}_{j\xi} \cdot \hat{\mathbf{A}}(\hat{\mathbf{R}}_{j\xi}) + \sum_{j=1}^{N_n} \frac{Z_j^2 e^2}{2M_j} |\hat{\mathbf{A}}(\hat{\mathbf{R}}_{j\xi})|^2, \end{aligned} \quad (5.7)$$

$$\begin{aligned} \hat{H}_{\text{Coul}\xi\xi'} = & \sum_{i=1}^{N_e} \sum_{i'=1}^{N_e} \frac{e^2}{4\pi\epsilon_0 |\hat{\mathbf{r}}_{i\xi} - \hat{\mathbf{r}}_{i'\xi'}|} - \sum_{i=1}^{N_e} \sum_{j=1}^{N_n} \frac{Z_j e^2}{4\pi\epsilon_0 |\hat{\mathbf{r}}_{i\xi} - \hat{\mathbf{R}}_{j\xi'}|} - \sum_{i=1}^{N_e} \sum_{j=1}^{N_n} \frac{Z_j e^2}{4\pi\epsilon_0 |\hat{\mathbf{r}}_{i\xi'} - \hat{\mathbf{R}}_{j\xi}|} \\ & + \sum_{j=1}^{N_n} \sum_{j'=1}^{N_n} \frac{Z_j Z_{j'} e^2}{4\pi\epsilon_0 |\hat{\mathbf{R}}_{j\xi} - \hat{\mathbf{R}}_{j'\xi'}|}, \end{aligned} \quad (5.8)$$

with m_e , $-e$, $\hat{\mathbf{r}}_{i\xi}$ and $\hat{\mathbf{p}}_{i\xi}$ the observable rest mass, the charge and the operators representing the position $\mathbf{r}_{i\xi}$ and canonical linear momentum $\mathbf{p}_{i\xi}$ of the i th electron in the ξ th molecule; M_j , $Z_j e$, $\hat{\mathbf{R}}_{j\xi}$ and $\hat{\mathbf{P}}_{j\xi}$ the observable rest mass, the charge and the operators representing the position $\mathbf{R}_{j\xi}$ and canonical linear momentum $\mathbf{P}_{j\xi}$ of the j th nucleus in the ξ th molecule. We have refrained from including in \hat{H} terms representing the Coulomb self energies of the electrons and nuclei which are diverging constants, as well as mass-renormalisation counter terms that arise from our use of the observable rather than bare masses of the electrons and nuclei.

We now invoke the clamped nucleus approximation, wherein the nuclei are held *fixed* by taking $M_j \rightarrow \infty$ and setting $\hat{\mathbf{R}}_{j\xi} \rightarrow \mathbf{R}_{j\xi}$ with the latter treated classically and considered to be independent of time t . We orient the nuclear skeletons of the molecules identically.

5.2.2 In the absence of \hat{V} : free propagation

It is instructive, albeit artificial, to temporarily *neglect* the interaction between the light and the molecules as well as the Coulomb interactions between the molecules. Within the present subsection, let us thus set $\hat{V} = 0$ so that $\hat{H} = \hat{H}_0$ and the light and the individual molecules evolve independently of one another.

Assuming that the eigenspectrum of the operator $\hat{H}_{\text{mol}\xi}$ representing the Hamiltonian of the ξ th molecule is known:

$$\hat{H}_{\text{mol}\xi}|k_\xi\rangle = \hbar\omega_{k_\xi}|k_\xi\rangle, \quad (5.9)$$

with the eigenstates $|k_\xi\rangle$ being complete ($\sum_{k_\xi=0}^\infty |k_\xi\rangle\langle k_\xi| = 1$) and orthonormal ($\langle k_\xi|k_{\xi'}\rangle = \delta_{\xi\xi'}$) and where $k = 0$ in particular denotes the molecular ground state, we have that the eigenspectrum of \hat{H}_0 is

$$\hat{H}_0|s^{(0)}\rangle = \hbar\omega_s^{(0)}|s^{(0)}\rangle, \quad (5.10)$$

with

$$\left\{ |s^{(0)}\rangle \right\} = \left\{ |\{n_{\mathbf{k}\sigma}\}\rangle \prod_{\xi=1}^{N_{\text{mol}}} |k_\xi\rangle \right\}, \quad (5.11)$$

$$\left\{ \hbar\omega_s^{(0)} \right\} = \left\{ \sum_{\mathbf{k}} \sum_{\sigma} \hbar c|\mathbf{k}|n_{\mathbf{k}\sigma} + \sum_{\xi=1}^{N_{\text{mol}}} \hbar\omega_{k_\xi} + \mathcal{Z}^{(0)} \right\}. \quad (5.12)$$

Of particular interest to us at present is the eigenstate $|(n_{\mathbf{k}\sigma}, 0)^{(0)}\rangle$ of \hat{H}_0 in which a single circularly polarised plane-wave mode, of wavevector \mathbf{k} and polarisation parameter σ , possesses $n_{\mathbf{k}\sigma}$ photons whilst every other mode is devoid of excitation and each of the molecules occupies its ground state:

$$|(n_{\mathbf{k}\sigma}, 0)^{(0)}\rangle = |n_{\mathbf{k}\sigma}\rangle \prod_{\xi=1}^{N_{\text{mol}}} |0_\xi\rangle, \quad (5.13)$$

as follows from (5.11). The associated eigenvalue $\hbar\omega_{(n_{\mathbf{k}\sigma}, 0)}^{(0)}$ is comprised of the energies $\hbar c|\mathbf{k}|$ of the photons, the ground state energies $\hbar\omega_{0\xi}$ of the molecules and the electromagnetic vacuum energy $\mathcal{Z}^{(0)}$:

$$\hbar\omega_{(n_{\mathbf{k}\sigma}, 0)}^{(0)} = \hbar c|\mathbf{k}|n_{\mathbf{k}\sigma} + \sum_{\xi=1}^{N_{\text{mol}}} \hbar\omega_{0\xi} + \mathcal{Z}^{(0)}, \quad (5.14)$$

as follows from (5.12). Let us now superpose such eigenstates to form a state $|\Psi\rangle$ in which the circularly polarised plane-wave mode of wavevector \mathbf{k} and polarisation parameter σ occupies a coherent state of parameter $\tilde{\alpha}_{\mathbf{k}\sigma}$ whilst each of the molecules occupies its ground state:

$$|\Psi\rangle = \exp(-|\tilde{\alpha}_{\mathbf{k}\sigma}|^2/2) \sum_{n_{\mathbf{k}\sigma}=0}^{\infty} \frac{\tilde{\alpha}_{\mathbf{k}\sigma}^{n_{\mathbf{k}\sigma}}}{\sqrt{n_{\mathbf{k}\sigma}!}} \exp[-i\omega_{(n_{\mathbf{k}\sigma}, 0)}^{(0)}t] |(n_{\mathbf{k}\sigma}, 0)^{(0)}\rangle. \quad (5.15)$$

We take $\tilde{\alpha}_{\mathbf{k}\sigma}$ to be such that the light is suitably ‘weaker’ than the Coulomb fields that bind the molecules together. The significance of $|\Psi\rangle$ is manifest in the expectation value

$$\langle \Psi | \hat{\mathbf{A}} | \Psi \rangle = \Re \left\{ \tilde{\mathbf{A}}_0 \exp [i (\mathbf{k} \cdot \mathbf{r} - c|\mathbf{k}|t)] \right\}, \quad (5.16)$$

where $\tilde{\mathbf{A}}_0 = \tilde{\mathbf{e}}_{\mathbf{k}\sigma} \tilde{\alpha}_{\mathbf{k}\sigma} \sqrt{2\hbar/\epsilon_0 c |\mathbf{k}| V}$. The form seen in (5.16) resembles that of a classical plane wave propagating freely in the strict absence of charge. This is entirely natural, of course: as $\hat{V} = 0$, the light does not ‘see’ the medium.

5.2.3 In the presence of \hat{V} : refraction

Let us now incorporate the interaction between the light and the molecules as well as the Coulomb interactions between the molecules. Thus, we take $\hat{H} = \hat{H}_0 + \hat{V}$ and examine how optical refraction enters into the results presented in §5.2.2 through our inclusion of \hat{V} , the influence of which we treat in a perturbative manner, working to order e^2 .

Taking each molecule to be smaller than the free-space wavelength $2\pi/|\mathbf{k}|$ associated with the circularly polarised plane-wave mode of wavevector \mathbf{k} and polarisation parameter σ and the molecular number density N_{mol}/V to be small, we find that the perturbed eigenvalue $\hbar\omega_{(n_{\mathbf{k}\sigma},0)}$ is

$$\hbar\omega_{(n_{\mathbf{k}\sigma},0)} = \frac{\hbar c |\mathbf{k}| n_{\mathbf{k}\sigma}}{n_p(c|\mathbf{k}|)} + \sum_{\xi=1}^{N_{\text{mol}}} \hbar\omega_{0\xi} + \mathcal{Y} + \mathcal{Z}, \quad (5.17)$$

where we have identified the reciprocal $1/n_p(c|\mathbf{k}|)$ of the phase refractive index $n_p(c|\mathbf{k}|)$ supported by the medium at angular frequency $c|\mathbf{k}|$:

$$\frac{1}{n_p(c|\mathbf{k}|)} \approx 1 - \frac{\tilde{\mathbf{e}}_{\mathbf{k}\sigma(a)}^* \tilde{\mathbf{e}}_{\mathbf{k}\sigma(b)} N_{\text{mol}}}{2\epsilon_0 V} \left[\tilde{\alpha}_{(ab)}(c|\mathbf{k}|) + \tilde{\zeta}_{(abc)}(c|\mathbf{k}|) \hat{k}_{(c)} \right], \quad (5.18)$$

\mathcal{Y} is due to the Coulomb energies between the molecules:

$$\mathcal{Y} = \langle (n_{\mathbf{k}\sigma}, 0)^{(0)} | \sum_{\xi=1}^{N_{\text{mol}}-1} \sum_{\xi'=1}^{N_{\text{mol}}} \hat{H}_{\text{Coul}\xi\xi'} | (n_{\mathbf{k}\sigma}, 0)^{(0)} \rangle \quad (5.19)$$

and \mathcal{Z} is comprised of diverging terms, including $\mathcal{Z}^{(0)}$, that are independent of the state of the light and do not affect our present discussions: $\mathcal{Z} - \mathcal{Z}^{(0)}$ is attributable to the radiative self-interactions of the electrons. To obtain these results, we have considered electric dipole, electric quadrupole and magnetic dipole contributions to the multipolar expansion of the ‘ $\mathbf{p} \cdot \mathbf{A}$ ’ terms in \hat{V} and have retained only the electric-dipole / electric-dipole, electric-dipole / electric quadrupole and electric-dipole / magnetic-dipole contributions to $\hbar\omega_{(n_{\mathbf{k}\sigma},0)}$ that result. We found it possible and necessary, however, to calculate the contributions made to $\hbar\omega_{(n_{\mathbf{k}\sigma},0)}$ by the ‘ $|\mathbf{A}|^2$ ’ terms in \hat{V} in an exact manner.

Comparing $\hbar\omega_{(n_{\mathbf{k}\sigma},0)}$ and $\hbar\omega_{(n_{\mathbf{k}\sigma},0)}^{(0)}$, we see that inclusion of \hat{V} has rescaled the energies $\hbar c |\mathbf{k}|$ of the photons by a factor of $1/n_p(c|\mathbf{k}|)$ and shifted the energy of the system ‘light+medium’ by

$\mathcal{Y} + \mathcal{Z} - \mathcal{Z}^{(0)}$. Thus, we identify an *interaction energy* Σ shared between the light and the medium as

$$\begin{aligned}\Sigma &= \frac{\hbar c |\mathbf{k}| n_{\mathbf{k}\sigma}}{n_p(c|\mathbf{k}|)} - \hbar c |\mathbf{k}| n_{\mathbf{k}\sigma} \\ &\approx -\frac{\hbar c |\mathbf{k}| n_{\mathbf{k}\sigma} \tilde{e}_{\mathbf{k}\sigma(a)}^* \tilde{e}_{\mathbf{k}\sigma(b)} N_{\text{mol}}}{2\epsilon_0 V} \left[\tilde{\alpha}_{(ab)}(c|\mathbf{k}|) + \tilde{\zeta}_{(abc)}(c|\mathbf{k}|) \hat{k}_{(c)} \right].\end{aligned}\quad (5.20)$$

In a classical picture, we might associate Σ with the oscillations induced in the charge and current distributions of the molecules by the light as the light propagates through the medium. We attribute optical refraction to Σ in that

$$\begin{aligned}n_p(c|\mathbf{k}|) &\approx 1 - \frac{\Sigma}{\mathcal{W}} \\ &\approx 1 + \frac{\tilde{e}_{\mathbf{k}\sigma(a)}^* \tilde{e}_{\mathbf{k}\sigma(b)} N_{\text{mol}}}{2\epsilon_0 V} \left[\tilde{\alpha}_{(ab)}(c|\mathbf{k}|) + \tilde{\zeta}_{(abc)}(c|\mathbf{k}|) \hat{k}_{(c)} \right]\end{aligned}\quad (5.21)$$

with $\mathcal{W} = \langle n_{\mathbf{k}\sigma} | \hat{H}_{\text{rad}} | n_{\mathbf{k}\sigma} \rangle - \mathcal{Z}^{(0)} = \hbar c |\mathbf{k}| n_{\mathbf{k}\sigma}$ here the unperturbed energy of the photons. That is, the deviation in phase speed of the light away from c is dictated by the ratio of Σ to \mathcal{W} .

Our identification of $n_p(c|\mathbf{k}|)$ may be justified through consideration of the perturbed state

$$|\Psi\rangle = \exp(-|\tilde{\alpha}_{\mathbf{k}\sigma}|^2/2) \sum_{n_{\mathbf{k}\sigma}=0}^{\infty} \frac{\tilde{\alpha}_{\mathbf{k}\sigma}^{n_{\mathbf{k}\sigma}}}{\sqrt{n_{\mathbf{k}\sigma}!}} \exp[-i\omega_{(n_{\mathbf{k}\sigma},0)}t] | (n_{\mathbf{k}\sigma}, 0) \rangle, \quad (5.22)$$

in which

$$\langle \Psi | \hat{\mathbf{A}} | \Psi \rangle \approx \Re \left(\tilde{\mathbf{A}}_0 \exp \{ i [n_p(c|\mathbf{k}_0|) \mathbf{k}_0 \cdot \mathbf{r} - c|\mathbf{k}_0|t] \} \right) \quad (5.23)$$

where $\mathbf{k}_0 = \mathbf{k}/n_p(c|\mathbf{k}|)$. The form seen in (5.23) once more resembles that of a classical plane wave, but propagating now with a phase speed $c/n_p(c|\mathbf{k}_0|)$, as desired.

5.2.4 Natural optical rotations and helicity

Here, we consider the natural optical rotation exhibited by a transparent fluid of chiral molecules, a phenomenon first observed in liquid turpentine, by Biot [25]. At any given t , the electric field vectors and magnetic flux density pseudovectors of the light are seen to twist *about the direction of propagation*. Hence, the sense of rotation relative to space is itself reversed upon reversal of the direction of propagation, as is depicted in figure 5.3. This is reminiscent of a Heaviside-Larmor rotation (2.1) and, indeed, we find that such natural optical rotations can be attributed explicitly to the helicity of the light, as follows.

We model the medium by taking isotropic averages of the results presented in §5.2.3 and obtain

$$\Sigma \approx \frac{N_{\text{mol}}}{3\epsilon_0 V} \left[-\frac{1}{2} \alpha_{(aa)}(c|\mathbf{k}|) \mathcal{W} + \frac{1}{c} G'_{(aa)}(c|\mathbf{k}|) |\mathbf{k}| \mathcal{H} \right], \quad (5.24)$$

$$n_p(c|\mathbf{k}_0|) \approx 1 + \frac{N_{\text{mol}}}{3\epsilon_0 V} \left[\frac{1}{2} \alpha_{(aa)}(c|\mathbf{k}_0|) - \frac{1}{c} G'_{(aa)}(c|\mathbf{k}_0|) |\mathbf{k}_0| \frac{\mathcal{H}}{\mathcal{W}} \right], \quad (5.25)$$

where $\mathcal{H} = \langle n_{\mathbf{k}\sigma} | \hat{\mathcal{H}} | n_{\mathbf{k}\sigma} \rangle$ is the unperturbed *helicity* of the photons. It is the sensitivity to \mathcal{H} exhibited by Σ and $n_p(c|\mathbf{k}_0|)$ that gives rise to circular birefringence and hence, the natural optical rotation: as \mathcal{H} differs for left- and right-handed circular polarisations, so too do Σ and $n_p(c|\mathbf{k}_0|)$ and it follows that

$$\theta(c|\mathbf{k}_0|) \approx -\frac{N_{\text{mol}} G'_{(aa)}(c|\mathbf{k}_0|) |\mathbf{k}_0| l}{3\epsilon_0 c V}, \quad (5.26)$$

which is the well-known result due to Rosenfeld and Condon [12, 25]. Like \mathcal{H} , from which it derives, $\theta(c|\mathbf{k}_0|)$ is independent of the direction of propagation, as it should be. The sign of the trace $G'_{(aa)}(c|\mathbf{k}_0|)$ is dictated by the chirality of the molecules, which in turn dictates the sign of $\theta(c|\mathbf{k}_0|)$.

That Σ should depend upon the chiralities of the photons and the molecules, as embodied by \mathcal{H} and $G'_{(aa)}$, seems natural, perhaps, when we recall the classical picture suggested earlier wherein Σ is associated with the oscillations induced in the charge and current distributions of molecules by the light as the light propagates through the medium. In general, the twisting electric field vectors and magnetic flux density pseudovectors associated with one handedness of circular polarisation will be better suited to induce these oscillations in a given chiral molecule than those associated with the opposite handedness of circular polarisation. To give an analogy: the energies required to ‘fit’ opposite gloves onto a given human hand will, of course, differ!

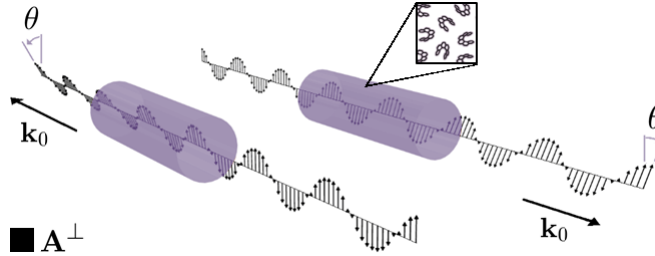


Figure 5.3: The natural optical rotations exhibited by a transparent fluid of chiral molecules tend to cancel upon reversal of the direction of propagation.

5.2.5 Faraday optical rotations and spin

In his quest to demonstrate a connection between electromagnetism and light, Faraday discovered the effect that now bears his name [25]: a Faraday optical rotation is exhibited by *any* transparent medium in the presence of a static magnetic field. Here, we consider the Faraday optical rotation exhibited by a transparent fluid of achiral molecules or atoms in the presence of a weak, uniform, static magnetic flux density \mathbf{B}_0 which defines a unique direction, thus rendering the fluid a uniaxial medium. At any given t , the electric field vectors and magnetic flux density pseudovectors of the light are seen to twist *about* \mathbf{B}_0 , in a manner that respects their solenoidal character. Hence, the sense of rotation relative to space is unchanged upon reversal of the direction of propagation as depicted in figure 5.4. This is reminiscent of a van Enk-Nienhuis-Barnett rotation (the infinitesimal form of which is seen in (4.61)) and indeed, we find that such Faraday optical rotations can be attributed explicitly to the spin of the light, as follows.

The effect of \mathbf{B}_0 is to perturb the polarisabilities of the molecules or atoms such that

$$\begin{aligned}\alpha_{(ab)} &\rightarrow \alpha_{(ab)} + \alpha_{(abc)}^{(m)} B_{0(c)} \\ \alpha'_{(ab)} &\rightarrow \alpha'_{(ab)} + \alpha'_{(abc)}^{(m)} B_{0(c)},\end{aligned}\quad (5.27)$$

for example, to first order in \mathbf{B}_0 . Explicit expressions of relevance here can be found in Barron's book [25]. Neglecting the permanent magnetic multipole moments of the molecules or atoms, we model the medium by taking isotropic averages of the results presented in §5.2.3, thus obtaining

$$\Sigma \approx \frac{N_{\text{mol}}}{3\epsilon_0 V} \left[-\frac{1}{2} \alpha_{(aa)} (c|\mathbf{k}|) \mathcal{W} - \frac{1}{4} \epsilon_{(abc)} \alpha_{(abc)}^{(m)} (c|\mathbf{k}|) c|\mathbf{k}| \mathbf{B}_0 \cdot \mathcal{S} \right], \quad (5.28)$$

$$n_p (c|\mathbf{k}_0|) \approx 1 + \frac{N_{\text{mol}}}{3\epsilon_0 V} \left[\frac{1}{2} \alpha_{(aa)} (c|\mathbf{k}_0|) + \frac{1}{4} \epsilon_{(abc)} \alpha_{(abc)}^{(m)} (c|\mathbf{k}_0|) c|\mathbf{k}_0| \mathbf{B}_0 \cdot \frac{\mathcal{S}}{\mathcal{W}} \right], \quad (5.29)$$

to leading order, where $\mathcal{S} = \langle n_{\mathbf{k}\sigma} | \hat{\mathbf{S}} | n_{\mathbf{k}\sigma} \rangle$ is the unperturbed *spin* of the photons. It is the sensitivity to \mathcal{S} exhibited by Σ and $n_p (c|\mathbf{k}_0|)$ that gives rise to circular birefringence and hence, the Faraday optical rotation: as \mathcal{S} differs for left- and right-handed circular polarisations, so too do Σ and $n_p (c|\mathbf{k}_0|)$ and it follows that

$$\theta (c|\mathbf{k}_0|) \approx \frac{N_{\text{mol}} \epsilon_{(abc)} \alpha_{(abc)}^{(m)} (c|\mathbf{k}_0|) l}{12\epsilon_0 V} \mathbf{B}_0 \cdot \mathbf{k}_0, \quad (5.30)$$

which is the accepted result due to Serber, Buckingham and Stephens [25]. Like \mathcal{S} , from which it derives, $\theta (c|\mathbf{k}_0|)$ is dependent upon the direction of propagation, with the angular dependence familiar from Verdet's empirical law [25] emerging here through the dot product $\mathbf{B}_0 \cdot \mathbf{k}_0$.

Thus concludes our present consideration of optical refraction and optical rotation. It remains to calculate the perturbed eigenstates $|(n_{\mathbf{k}\sigma}, 0)\rangle$ and, moreover, to understand how absorption fits into our picture. Of course, one can also imagine modifying and / or extending our calculations to describe other media, for example semiconductors, metals, plasmas etc. These are tasks for future research.

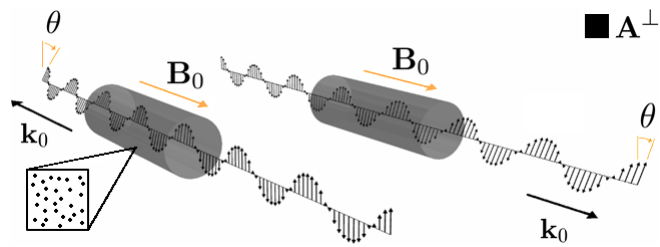


Figure 5.4: The Faraday optical rotations exhibited by a transparent fluid of achiral molecules or atoms tend to add upon reversal of the direction of propagation. This behaviour, which derives from the properties of spin, should be contrasted with the behaviour depicted in figure 5.3, which derives from the properties of helicity.

5.3 Differential scattering

It is now well established in theory that optical activity in the *scattering* of light is exhibited naturally by chiral molecules [12, 25, 154–156] and can be induced additionally in all molecules and atoms by an applied static magnetic [25, 157] or electric [25, 158] field. The phenomenon permits the extraction of information about molecules and atoms that is not readily obtainable through optical rotation or its absorptive counterpart: circular dichroism, owing to the subtly different physical mechanism and greater geometrical freedom involved [12, 25].

Many manifestations of optical activity in light scattering have now been observed in experiment [25, 159–163]. Natural Raman optical activity in particular has been developed into an incisive spectroscopic tool which has been employed to study large biological molecules and even intact viruses [25, 159, 162, 163]. Owing primarily to the smallness of the effects involved, there remains much to be pursued, however. Natural Rayleigh optical activity for example has thus far resisted attempts to observe it in experiment [25, 164], in spite of potential applications such as the robust assignment of the absolute configurations of small chiral molecules [165].

The theoretical and experimental approaches undertaken to date towards the phenomenon have been concerned with the illumination of molecules or atoms by *single* plane (or quasi plane) waves² [12, 25, 154–163, 165]. I observe, however, that optical activity in light scattering can also be probed, in general, using other types of illuminating light and that this introduces new possibilities for the study of molecules and atoms. In the present section, we demonstrate this explicitly for natural Rayleigh optical activity which could be exploited as a new form of spectroscopy for chiral molecules through the use of illuminating light comprised of *two* plane waves that are counter propagating.

5.3.1 Natural Rayleigh optical activity

Consider $N_{\text{mol}} \gg 1$ chiral molecules located at fixed positions \mathbf{R}_ξ ($\xi = 1, \dots, N_{\text{mol}}$). Neglecting interactions between them and assuming an absence of applied static electric and magnetic fields, we take the molecules to be randomly orientated but otherwise identical. We suppose, however, that they are illuminated by weak, monochromatic, off-resonance light of angular frequency $\omega = c|\mathbf{k}|$ (in the visible or near infrared say) that is otherwise freely propagating and the length scale $2\pi/|\mathbf{k}|$ associated with which is larger than each molecule. The electric field \mathbf{E} and magnetic flux density \mathbf{B} comprising the illuminating light are described by (1.75)-(1.80): we regard the illuminating light as being an externally imposed influence acting upon the molecules to which they are introduced in an adiabatic manner.

The oscillations induced by the illuminating light in the charge and current distributions of the molecules generate Rayleigh *scattered* light in turn [12, 25], the electric field $\mathbf{E}_{\text{scatt}}$ and magnetic flux density $\mathbf{B}_{\text{scatt}}$ of which may be calculated using the the solutions seen in (1.87) and (1.88) together with the results presented in §1.4. At a position $\mathbf{r} = \mathbf{R}$ of fixed magnitude $|\mathbf{R}| \gg |\mathbf{R}_\xi|, 2\pi/|\mathbf{k}|$, we find then

²In experiment, single beams of light that resemble plane waves.

that

$$\mathbf{E}_{\text{scatt}} \approx \Re \left[\tilde{\mathbf{E}}_{\text{scatt}} \exp(-i\omega t) \right], \quad (5.31)$$

$$\mathbf{B}_{\text{scatt}} \approx \Re \left[\tilde{\mathbf{B}}_{\text{scatt}} \exp(-i\omega t) \right], \quad (5.32)$$

with the components $\tilde{E}_{\text{scatt}(a)}$ and $\tilde{B}_{\text{scatt}(a)}$ of the complex quantities $\tilde{\mathbf{E}}_{\text{scatt}}$ and $\tilde{\mathbf{B}}_{\text{scatt}}$ related to the oscillations in the charge and current distributions of the molecules as

$$\begin{aligned} \tilde{E}_{\text{scatt}(a)} = & \frac{\omega^2 \mu_0}{4\pi |\mathbf{R}|} \sum_{\xi=1}^{N_{\text{mol}}} \exp(i|\mathbf{k}||\mathbf{R} - \mathbf{R}_{\xi}|) \left\{ \tilde{\mu}_{\xi(a)} - \hat{R}_{(a)} \hat{R}_{(b)} \tilde{\mu}_{\xi(b)} \right. \\ & \left. - \hat{R}_{(b)} \frac{1}{c} \epsilon_{(abc)} \tilde{m}'_{\xi(c)} - \frac{i|\mathbf{k}|}{3} \hat{R}_{(b)} \left[\tilde{\Theta}_{\xi(ab)} - \hat{R}_{(a)} \hat{R}_{(c)} \tilde{\Theta}_{\xi(bc)} \right] \right\}, \end{aligned} \quad (5.33)$$

$$\tilde{B}_{\text{scatt}(a)} = \frac{1}{c} \epsilon_{(abc)} \hat{R}_{(b)} \tilde{E}_{\text{scatt}(c)}. \quad (5.34)$$

The intensity $I = I(\hat{\mathbf{R}})$ of the scattered light seen at \mathbf{R} is

$$I = \left\langle \left| \frac{1}{\mu_0} \mathbf{E}_{\text{scatt}} \times \mathbf{B}_{\text{scatt}} \right| \right\rangle, \quad (5.35)$$

with the indicated isotropic rotational average [12, 25] included to account for the random orientations of the molecules. Making no assumptions beyond those described above whilst rejecting ‘ A^2 ’, ‘ AG ’ and ‘ G'^2 ’ contributions, which are anticipated to be some three orders of magnitude smaller than the smallest contributions thus retained [25], we obtain

$$\begin{aligned} I \approx & \sum_{\xi=1}^{N_{\text{mol}}} \frac{K}{|\mathbf{R}|^2} \left\{ 2\mathcal{A} \overline{w}_E(\mathbf{R}_{\xi}) + 2\mathcal{B} \hat{R}_{(a)} \hat{R}_{(b)} \overline{T}_E^{ab}(\mathbf{R}_{\xi}) \right. \\ & \left. + \omega \left[\mathcal{C} \overline{h}(\mathbf{R}_{\xi}) + 2\mathcal{D} \hat{\mathbf{R}} \cdot \overline{\mathbf{s}}_E(\mathbf{R}_{\xi}) + \mathcal{E} \hat{R}_{(a)} \hat{R}_{(b)} \overline{n}_{(ab)}(\mathbf{R}_{\xi}) + \mathcal{F} \hat{R}_{(a)} \hat{R}_{(b)} \overline{x}_{(ab)}(\mathbf{R}_{\xi}) \right] \right\}, \end{aligned} \quad (5.36)$$

where $K = \mu_0^2 c \omega^4 / 2880 \pi^2$. Both \mathcal{A} and \mathcal{B} (explicit expressions given below) are equal for opposite molecular enantiomers and are thus insensitive to the chirality of the molecules, whilst $\overline{w}_E = \overline{w}_E(\mathbf{r})$ and $\overline{T}_E^{ab} = \overline{T}_E^{ab}(\mathbf{r})$ can be identified as being the cycle-averaged values taken by the electric pieces of the energy density w and the linear momentum flux density components T^{ab} of the illuminating light as

$$\overline{w}_E = \overline{\epsilon_0 \mathbf{E} \cdot \mathbf{E} / 2}, \quad (5.37)$$

$$\overline{T}_E^{ab} = \overline{\epsilon_0 [\delta_{(ab)} \mathbf{E} \cdot \mathbf{E} - 2E_{(a)} E_{(b)}] / 2}. \quad (5.38)$$

In contrast \mathcal{C} , \mathcal{D} , \mathcal{E} and \mathcal{F} (explicit expressions given below) each assume equal magnitudes but opposite signs for opposite molecular enantiomers and so *are* sensitive to the chirality of the molecules, whilst \overline{h} , $\overline{\mathbf{s}}_E$ and $\overline{n}_{(ab)}$ can be identified as being the cycle-averaged values taken by the helicity density h , the electric piece of the spin density \mathbf{s} and the ab infra zilch density $n_{(ab)}$ of the illuminating

light as

$$\bar{h} = \overline{\epsilon_0 c (\mathbf{A}^\perp \cdot \mathbf{B} - \mathbf{C}^\perp \cdot \mathbf{E}) / 2}, \quad (5.39)$$

$$\bar{s}_E = \overline{\epsilon_0 \mathbf{E} \times \mathbf{A}^\perp / 2}, \quad (5.40)$$

$$\bar{n}_{(ab)} = \overline{\epsilon_0 c \left[\delta_{(ab)} (\mathbf{A}^\perp \cdot \mathbf{B} - \mathbf{C}^\perp \cdot \mathbf{E}) - A_{(a)}^\perp B_{(b)} - A_{(b)}^\perp B_{(a)} + C_{(a)}^\perp E_{(b)} + C_{(b)}^\perp E_{(a)} \right] / 2}. \quad (5.41)$$

The quantity $\bar{x}_{ab} = \bar{x}_{ab}(\mathbf{r})$ is unfamiliar to us, being

$$\bar{x}_{(ab)} = \overline{\epsilon_0 c \left\{ \partial_d \left[\epsilon_{(acd)} A_{(b)}^\perp A_{(c)}^\perp + \epsilon_{(bcd)} A_{(a)}^\perp A_{(c)}^\perp \right] \right\} / 2}, \quad (5.42)$$

which vanishes, in fact, for illuminating light comprised of a single plane wave, although it is non vanishing in general. We could have incorporated \bar{x}_{ab} into part of $\bar{n}_{(ab)}$ whilst retained the interpretation of the latter as being the cycle-averaged value taken by an ab infra zilch density, as $\bar{x}_{(ab)}$ is a total divergence which vanishes when integrated over all \mathbf{r} .

Our calculation differs from those that have been performed previously [12, 25, 154–156] in that the illuminating light here need not be comprised of a single plane wave of angular frequency ω but rather can be constructed from *any* superposition of such waves. Moreover, the molecules need not be distributed homogeneously and could instead be confined within a plane, for example. It should be noted, however, that (5.36) is not appropriate when the direction $\hat{\mathbf{R}}$ of observation coincides with the direction of propagation of a plane-wave component of the illuminating light, which will then interfere with the scattered light as Rayleigh scattering is a coherent process [12, 25]. Moreover, having been derived specifically for illuminating light that is (otherwise) freely propagating in accord with the charge-free Maxwell equations, (5.36) is not appropriate for illuminating light the electric field of which possesses a non-vanishing irrotational component, such as may be found in the near field of a radiating structure, for example. We have refrained from exhibiting a generalised structure factor (inter-molecule cross terms [12]) in (5.36) as it makes no contribution in the examples that follow and in other geometries besides.

Our general result (5.36) reveals in particular that natural Rayleigh optical activity, as manifest in I , can be utilised to extract information about the chirality of the molecules using essentially *any* type of illuminating light possessing non-vanishing helicity, spin and / or ab infra zilches. A single circularly polarised plane wave is, perhaps, the most obvious example of such light and is examined in §5.3.2. It is not the *only* one, however: as we will demonstrate in §5.3.3–§5.3.5, types of illuminating light comprised of *two* plane waves that are counter propagating can carry these angular momenta in novel ways and thus enable new possibilities. In identifying these, we were guided by symmetry considerations. In particular, it is necessary for \mathbf{E} and \mathbf{B} together with $\hat{\mathbf{R}}$ to be of chiral character in order that I itself be capable of distinguishing between opposite molecular enantiomers, as is inherent, of course, in (5.36).

Explicitly;

$$\mathcal{A} = 2(45a^2 + 13\beta^2), \quad (5.43)$$

$$\mathcal{B} = 2(45a^2 + \beta^2), \quad (5.44)$$

$$\mathcal{C} = 4(-45aG' - 13\beta_G^2 + \beta_A^2)/c, \quad (5.45)$$

$$\mathcal{D} = 8(-45aG' + 5\beta_G^2 + 3\beta_A^2)/c, \quad (5.46)$$

$$\mathcal{E} = 4(-45aG' - \beta_G^2 - 3\beta_A^2)/c, \quad (5.47)$$

$$\mathcal{F} = 16\beta_A^2/c, \quad (5.48)$$

with

$$a^2 = \alpha_{(aa)}(\omega)\alpha_{(bb)}(\omega)/9, \quad (5.49)$$

$$\beta^2 = [3\alpha_{(ab)}(\omega)\alpha_{(ab)}(\omega) - \alpha_{(aa)}(\omega)\alpha_{(bb)}(\omega)]/2, \quad (5.50)$$

$$aG' = \alpha_{(aa)}(\omega)G'_{(bb)}/9, \quad (5.51)$$

$$\beta_G^2 = [3\alpha_{(ab)}(\omega)G'_{(ab)}(\omega) - \alpha_{(aa)}(\omega)G'_{(bb)}(\omega)]/2, \quad (5.52)$$

$$\beta_A^2 = \omega\epsilon_{(abc)}\alpha_{(ad)}(\omega)A_{(bcd)}(\omega)/2. \quad (5.53)$$

a^2 and β^2 do *not* distinguish between opposite molecular enantiomers and are strictly positive. They can also be measured through a combination of optical refraction and depolarised Rayleigh scattering experiments [12, 25, 156]. β^2 is typically an order of magnitude smaller than a^2 [165] and vanishes entirely for an isotropic molecule [12, 25]. aG' , β_G^2 and β_A^2 *do* distinguish between opposite molecular enantiomers however, by taking on equal magnitudes but opposite signs³. aG' can also be measured through a combination of optical refraction and optical rotation experiments [12, 25, 156]. In contrast, β_G^2 and β_A^2 *cannot* be readily measured by other means. They are, therefore, quantities of *particular* interest [25, 165]. aG'/c , β_G^2/c and β_A^2/c are typically three to five orders of magnitude smaller than a^2 [12, 25].

5.3.2 Example zero: circularly polarised illuminating light

As a check on the validity of (5.36) and for comparison in what follows, let us begin now by following previous approaches [12, 25, 154–156] and considering illuminating light comprised of a single circularly polarised plane wave of amplitude E_0 propagating in the $+z$ direction as

$$\tilde{\mathbf{E}}_{\pm}^{(0)} = E_0(\hat{\mathbf{x}} \pm i\hat{\mathbf{y}}) \exp(i|\mathbf{k}|z), \quad (5.54)$$

$$\tilde{\mathbf{B}}_{\pm}^{(0)} = E_0(\mp i\hat{\mathbf{x}} + \hat{\mathbf{y}}) \exp(i|\mathbf{k}|z)/c, \quad (5.55)$$

where the upper and lower signs yield left- and right-handed circular polarisations. This is both the prototypical type of light possessing non-vanishing helicity, spin and *ab* infra zilches [37, 52] and the prototypical type of chiral light [25]: as time passes, \mathbf{E} and \mathbf{B} rotate with a phase that varies in z such that they trace out cylindrical helices, the chiralities of which differ for the upper and lower signs seen

³ β_G^2 and β_A^2 can be positive or negative, in spite of the misleading but standard notation [165].

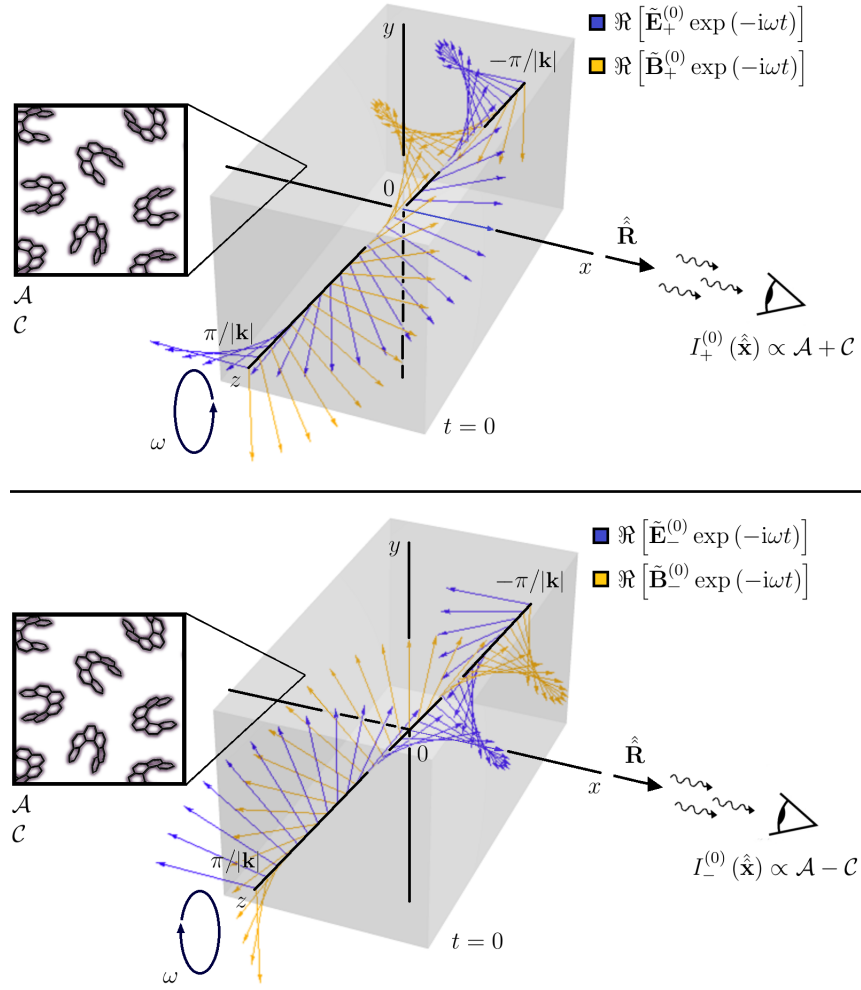


Figure 5.5: Illuminating light comprised of a single circularly polarised plane wave is scattered differently by the molecules depending upon whether it is left- or right-handed.

in (5.54) and (5.55). Accordingly

$$2\overline{w}_{E\pm}^{(0)} = \epsilon_0 E_0^2, \quad (5.56)$$

$$2\hat{R}_{(a)}\hat{R}_{(b)}\overline{T}_{E\pm}^{ab(0)} = \hat{R}_z^2 \epsilon_0 E_0^2, \quad (5.57)$$

$$\overline{h}_{\pm}^{(0)} = \pm \epsilon_0 E_0^2 / \omega, \quad (5.58)$$

$$2\hat{\mathbf{R}} \cdot \overline{\mathbf{s}}_{E\pm}^{(0)} = \pm \hat{R}_z \epsilon_0 E_0^2 / \omega, \quad (5.59)$$

$$\hat{R}_{(a)}\hat{R}_{(b)}\overline{n}_{(ab)\pm}^{(0)} = \pm \hat{R}_z^2 \epsilon_0 E_0^2 / \omega, \quad (5.60)$$

$$\hat{R}_{(a)}\hat{R}_{(b)}\overline{x}_{(ab)\pm}^{(0)} = 0, \quad (5.61)$$

where the upper and lower signs correspond to those seen in (5.54) and (5.55). Taking the molecules to be homogeneously distributed around the origin $\mathbf{r} = 0$, we find then that

$$I_{\pm}^{(0)} \approx \frac{\epsilon_0 K N E_0^2}{|\mathbf{R}|^2} \left[\mathcal{A} + \mathcal{B} \hat{R}_z^2 \pm \left(\mathcal{C} + \mathcal{D} \hat{R}_z + \mathcal{E} \hat{R}_z^2 \right) \right], \quad (5.62)$$

where the upper and lower signs again correspond to those seen in (5.54) and (5.55). Natural Rayleigh optical activity, as manifest in $I_{\pm}^{(0)}$, is thus attributable to the non-vanishing helicity, spin and *ab* infra zilches possessed by the illuminating light: $I_{\pm}^{(0)}$ differs for left- and right-handed circular polarisations because $\bar{h}_{\pm}^{(0)}$, $\bar{s}_{E\pm}^{(0)}$ and $\bar{n}_{(ab)\pm}^{(0)}$ do. For right-angled observation in particular, with $\hat{\mathbf{R}} = \hat{\mathbf{x}}$ say;

$$I_{\pm}^{(0)}(\hat{\mathbf{x}}) \approx \frac{\epsilon_0 K N E_0^2}{|\mathbf{R}|^2} (\mathcal{A} \pm \mathcal{C}). \quad (5.63)$$

This situation is depicted in figure 5.5.

This phenomenon is neatly quantified by the circular intensity difference $\Delta^{(0)} = \Delta^{(0)}(\hat{\mathbf{R}})$ defined as⁴ [155]

$$\Delta^{(0)}(\hat{\mathbf{R}}) = \frac{I_+^{(0)}(\hat{\mathbf{R}}) - I_-^{(0)}(\hat{\mathbf{R}})}{I_+^{(0)}(\hat{\mathbf{R}}) + I_-^{(0)}(\hat{\mathbf{R}})}, \quad (5.64)$$

which has equal magnitudes but opposite signs for opposite molecular enantiomers. Without loss of generality, we take $\hat{\mathbf{R}} = \sin \phi \hat{\mathbf{x}} + \cos \phi \hat{\mathbf{z}}$ and find that

$$\Delta^{(0)}(\sin \phi \hat{\mathbf{x}} + \cos \phi \hat{\mathbf{z}}) \approx \frac{\mathcal{C} + \mathcal{D} \cos \phi + \mathcal{E} \cos^2 \phi}{\mathcal{A} + \mathcal{B} \cos^2 \phi}, \quad (5.65)$$

which is the anticipated result [156]. For right-angled observation in particular [12, 25, 155], with $\hat{\mathbf{R}} = \hat{\mathbf{x}}$;

$$\begin{aligned} \Delta^{(0)}(\hat{\mathbf{x}}) &\approx \frac{\mathcal{C}}{\mathcal{A}} \\ &= \frac{2(-45aG' - 13\beta_G^2 + \beta_A^2)}{c(45a^2 + 13\beta^2)}. \end{aligned} \quad (5.66)$$

Owing primarily to the contribution made in the denominator by a^2 , $\Delta^{(0)}$ is rather small and, to the best of our knowledge, has not yet been observed in experiment for chiral molecules [25, 164]: calculated magnitudes of $\Delta^{(0)}$ typically lie between 10^{-6} and 10^{-4} [165]. We note, however, that experimental results have been reported for large biological structures [166].

5.3.3 Example one: superchiral illuminating light

Following a procedure recently suggested [83] and demonstrated [84] for luminescence-detected circular dichroism, we observe here the possibility of using so-called superchiral illuminating light, rather than illuminating light comprised of a single circularly polarised plane wave, to ensure that a *larger* fraction of I is sensitive to the chirality of the molecules, albeit at the expense of an overall reduction in I . We associate with this illuminating light, a quantity analogous to $\Delta^{(0)}(\hat{\mathbf{x}})$ that can be made larger in magnitude and may, therefore, be more amenable to observation in experiment.

Consider then a superposition of two circularly polarised plane waves of opposite handedness, the

⁴ $\Delta^{(0)}$ differs in sign from the circular intensity difference introduced by Barron and Buckingham in [155].

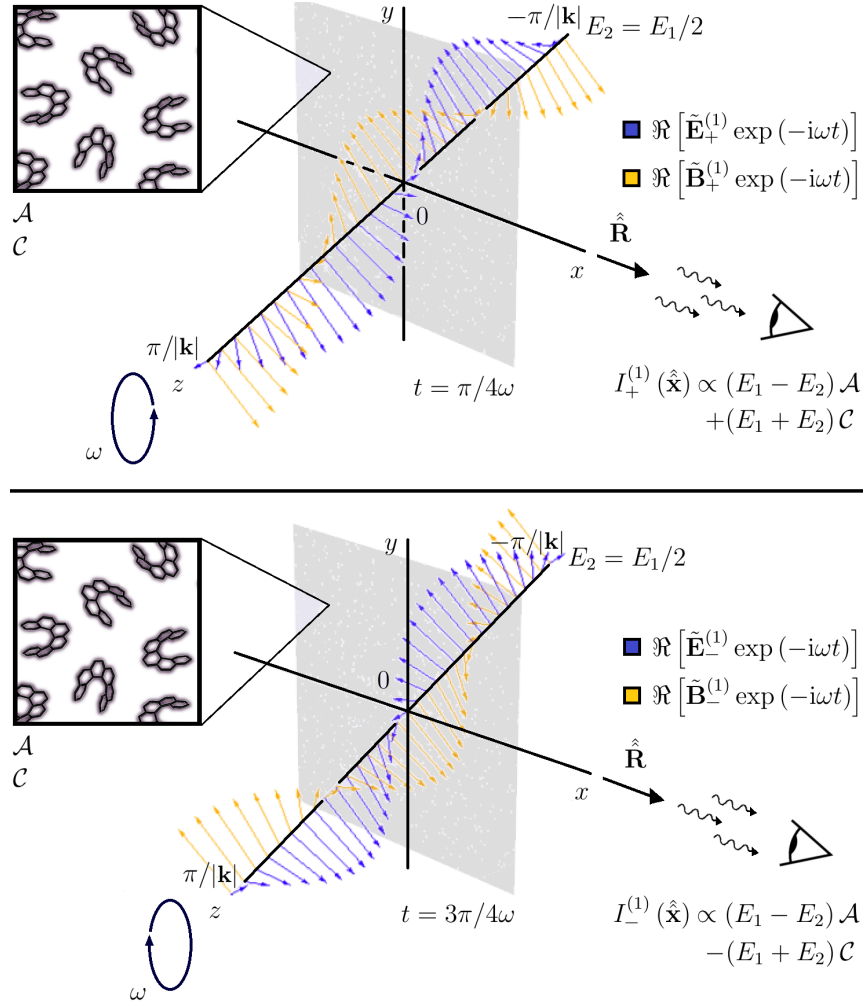


Figure 5.6: Superchiral illuminating light can be employed to ensure that a *larger* fraction of the intensity of the scattered light is sensitive to the chirality of the molecules, as compared to illuminating light comprised of a single circularly polarised plane wave.

first of which has amplitude $E_1/\sqrt{2}$ and propagates in the $+z$ direction whilst the second has amplitude $E_2/\sqrt{2} \neq E_1/\sqrt{2}$ and propagates in the $-z$ direction as

$$\tilde{\mathbf{E}}_{\pm}^{(1)} = E_1(\hat{\mathbf{x}} \pm i\hat{\mathbf{y}}) \exp(i|\mathbf{k}|z)/\sqrt{2} - E_2(\hat{\mathbf{x}} \pm i\hat{\mathbf{y}}) \exp(-i|\mathbf{k}|z)/\sqrt{2}, \quad (5.67)$$

$$\tilde{\mathbf{B}}_{\pm}^{(1)} = E_1(\mp i\hat{\mathbf{x}} + \hat{\mathbf{y}}) \exp(i|\mathbf{k}|z)/\sqrt{2} - E_2(\pm i\hat{\mathbf{x}} - \hat{\mathbf{y}}) \exp(-i|\mathbf{k}|z)/\sqrt{2}, \quad (5.68)$$

where the upper and lower signs distinguish the cases in which the first wave is left- or right-handed. This illuminating light is of course closely related to the light examined in §3.3.8. It is manifestly chiral as, at any given t , \mathbf{E} and \mathbf{B} twist helically in z , the sense of twist depending on $\text{sgn}(E_1 - E_2)$ whilst differing for the upper and lower signs seen in (5.67) and (5.68). As time passes, these helical patterns themselves rotate rigidly about the z axis, with the sense of rotation differing for the upper and lower signs in seen in (5.67) and (5.68). In the vicinity of the $z = 0$ plane, \mathbf{E} twists *unusually* fast in z , doing so at the cost of a reduced magnitude: a superoscillatory phenomenon [167]. In contrast, \mathbf{B} twists rather slowly in the vicinity of $z = 0$, but is of relatively large magnitude. The effect becomes more pronounced as $|E_1 - E_2| \rightarrow 0$.

Let us suppose then that the molecules are distributed homogeneously in the $z = 0$ plane about $\mathbf{r} = 0$. Adopting a right-angled observation geometry with $\hat{\mathbf{R}} = \hat{\mathbf{x}}$, we find that

$$I_{\pm}^{(1)}(\hat{\mathbf{x}}) \approx \frac{\epsilon_0 K N (E_1 - E_2)}{2|\mathbf{R}|^2} [\mathcal{A} (E_1 - E_2) \pm \mathcal{C} (E_1 + E_2)], \quad (5.69)$$

where the upper and lower signs correspond to those seen in (5.67) and (5.68). Comparing (5.69) with (5.63), we see that the chirally insensitive \mathcal{A} contribution to $I_{\pm}^{(1)}(\hat{\mathbf{x}})$ is reduced relative to the chirally sensitive \mathcal{C} contribution, albeit at the expense of an overall reduction in $I_{\pm}^{(1)}(\hat{\mathbf{x}})$. This occurs because the chirally insensitive \mathcal{A} contribution to $I_{\pm}^{(1)}(\hat{\mathbf{x}})$ is driven by \mathbf{E} alone through \overline{w}_E whilst the chirally sensitive \mathcal{C} contribution is driven instead by both \mathbf{E} and \mathbf{B} through \overline{h} : in the latter case, the unusually high degree of twisting exhibited by \mathbf{E} in the vicinity of the $z = 0$ plane, where the molecules reside, together with the relatively large magnitude of \mathbf{B} *compensates* somewhat for the small magnitude of \mathbf{E} there. The situation is depicted in figure 5.6.

We quantify this phenomenon through a generalised intensity difference $\chi^{(1)}$ defined as

$$\begin{aligned} \chi^{(1)} &= \frac{I_+^{(1)}(\hat{\mathbf{x}}) - I_-^{(1)}(\hat{\mathbf{x}})}{I_+^{(1)}(\hat{\mathbf{x}}) + I_-^{(1)}(\hat{\mathbf{x}})} \\ &\approx \frac{E_1 + E_2}{E_1 - E_2} \frac{\mathcal{C}}{\mathcal{A}} \\ &= \frac{E_1 + E_2}{E_1 - E_2} \Delta^{(0)}(\hat{\mathbf{x}}), \end{aligned} \quad (5.70)$$

which has equal magnitudes but opposite signs for opposite molecular enantiomers. This $\chi^{(1)}$ should be equal to or greater in magnitude than $\Delta^{(0)}(\hat{\mathbf{x}})$ and diverges, in fact, as $|E_1 - E_2| \rightarrow 0$ (and $I_{\pm}^{(1)}(\hat{\mathbf{x}}) \rightarrow 0$). In reality, such enhancements of $\chi^{(1)}$ relative to $\Delta^{(0)}$ are limited by contributions to the components $m'_{\xi(a)}$ of the magnetic dipole moments of the molecules induced by \mathbf{B} , which we have omitted explicitly from our analysis. Nevertheless, gains up to three orders of magnitude may be possible [12, 25, 83, 84].

5.3.4 Example two: σ - σ illuminating light

We observe now the possibility of using so-called σ - σ illuminating light, rather than illuminating light comprised of a single circularly polarised plane wave, to remove isotropic contributions to I whilst retaining both chirally insensitive and chirally sensitive anisotropic contributions. We associate with this illuminating light, a quantity analogous to $\Delta^{(0)}(\hat{\mathbf{x}})$ that is significantly larger in magnitude whilst offering different and perhaps more desirable information about the chirality of the molecules. This quantity may, therefore, be more suitable for observation in experiment.

Consider then a superposition of two circularly polarised plane waves of the same handedness and equal amplitude $E_0/\sqrt{2}$, the first of which propagates in the $+z$ direction whilst the second propa-

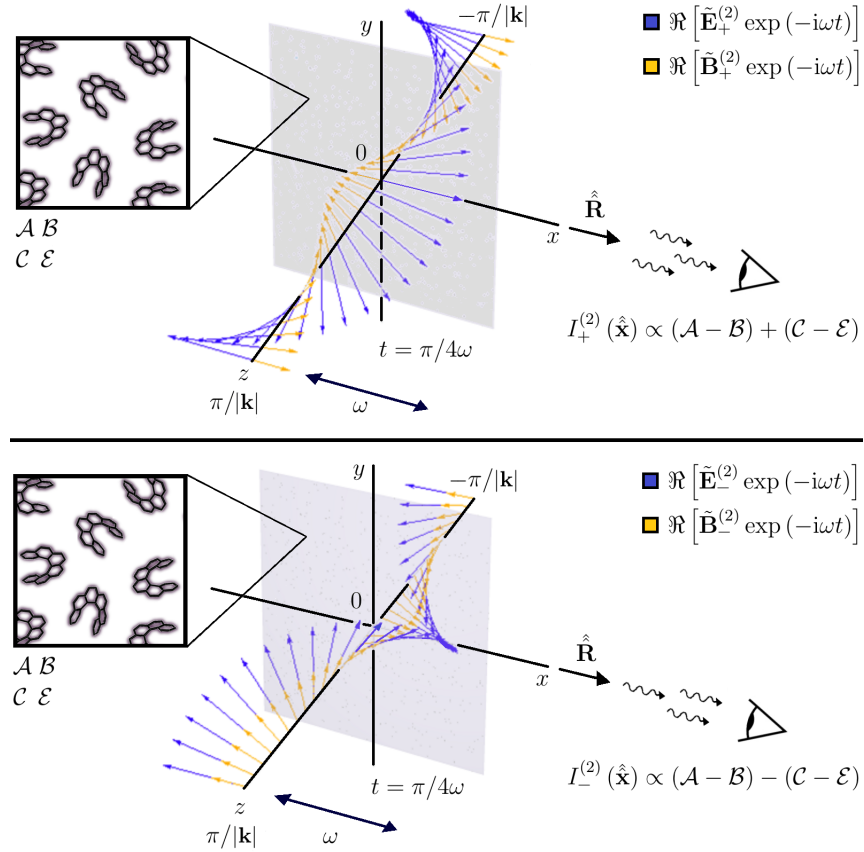


Figure 5.7: σ - σ illuminating light can be employed to ensure that the intensity of the scattered light contains no isotropic contributions whilst still being sensitive to the chirality of the molecules.

gates in the $-z$ direction as

$$\begin{aligned}\tilde{\mathbf{E}}_{\pm}^{(2)} &= E_0(\hat{\mathbf{x}} \pm i\hat{\mathbf{y}}) \exp(i|\mathbf{k}|z)/\sqrt{2} + E_0(\hat{\mathbf{x}} \mp i\hat{\mathbf{y}}) \exp(-i|\mathbf{k}|z)/\sqrt{2}, \\ \tilde{\mathbf{B}}_{\pm}^{(2)} &= E_0(\mp i\hat{\mathbf{x}} + \hat{\mathbf{y}}) \exp(i|\mathbf{k}|z)/\sqrt{2} + E_0(\mp i\hat{\mathbf{x}} - \hat{\mathbf{y}}) \exp(-i|\mathbf{k}|z)/\sqrt{2},\end{aligned}\quad (5.71)$$

where the upper and lower signs distinguish the cases in which the waves are left- or right-handed. This illuminating light is of course closely related to the light examined in §3.3.8. It is manifestly chiral, as \mathbf{E} and \mathbf{B} oscillate linearly and parallel to each other at each z whilst the plane in which they oscillate twists helically in z , the sense of twist differing for the upper and lower signs seen in equation (5.67) whilst \mathbf{E} lags or leads \mathbf{B} by a quarter cycle. In the $z = 0$ plane, \mathbf{E} and \mathbf{B} lie parallel to the x axis.

Let us suppose then that the molecules are distributed homogeneously in the $z = 0$ plane about $\mathbf{r} = 0$. Adopting a right-angled observation geometry with $\hat{\mathbf{R}} = \hat{\mathbf{x}}$, we find that

$$I_{\pm}^{(2)}(\hat{\mathbf{x}}) \approx \frac{\epsilon_0 K N E_0^2}{|\mathbf{R}|^2} [(\mathcal{A} - \mathcal{B}) \pm (\mathcal{C} - \mathcal{E})], \quad (5.72)$$

where the upper and lower signs correspond to those seen in (5.71). Evidently, $I_{\pm}^{(2)}(\hat{\mathbf{x}})$ contains *no* isotropic contributions, either chirally insensitive: a^2 , or chirally sensitive: aG' . It *does*, however,

possess non-vanishing anisotropic contributions, both chirally insensitive: β^2 , and chirally sensitive: β_G^2 and β_A^2 . This may be understood simply by recalling that an oscillating electric dipole moment radiates no energy on axis and so an isotropically polarisable molecular species would, to the order of present interest, exhibit no scattering in the direction $\hat{\mathbf{R}} = \hat{\mathbf{x}}$ of observation as the latter lies parallel to the (electric-dipole-inducing) \mathbf{E} vectors in the $z = 0$ plane where the molecules reside.

We quantify this phenomenon through a generalised intensity difference $\Lambda^{(2)}$ defined as

$$\begin{aligned}\Lambda^{(2)} &= \frac{I_+^{(2)}(\hat{\mathbf{x}}) - I_-^{(2)}(\hat{\mathbf{x}})}{I_+^{(2)}(\hat{\mathbf{x}}) + I_-^{(2)}(\hat{\mathbf{x}})} \\ &\approx \frac{\mathcal{C} - \mathcal{E}}{\mathcal{A} - \mathcal{B}} \\ &= \frac{2(\beta_A^2 - 3\beta_G^2)}{3c\beta^2},\end{aligned}\tag{5.73}$$

which has equal magnitudes but opposite signs for opposite molecular enantiomers. This $\Lambda^{(2)}$ should be larger than $\Delta^{(0)}(\hat{\mathbf{x}})$ by around two orders of magnitude [165] owing to the absence of a contribution from a^2 in the denominator. Moreover, $\Lambda^{(2)}(\hat{\mathbf{x}})$ offers different and perhaps more desirable information about the chirality of the molecules than $\Delta^{(0)}(\hat{\mathbf{x}})$ as its numerator is comprised solely of the quantities β_G^2 and β_A^2 of particular interest. We note that $\Lambda^{(2)}$ is -1 times the familiar depolarised right-angled circular intensity difference [12, 25]. The latter, however, requires analysed measurements of the intensities of scattered light polarised perpendicular to the scattering plane and is prone to spurious effects [25], owing to the relatively large intensities of scattered light polarised parallel to the scattering plane. In contrast, $\Lambda^{(2)}$ requires measurement only of *unanalysed* scattered intensities and should, therefore, be robust in this regard. Theoretical predictions of the variation of the familiar depolarised right-angled circular intensity difference (and hence, $\Lambda^{(2)}$) with frequency for various molecules can be seen in the work of Züber, Wipf and Beratan [165].

5.3.5 Example three: lin \perp lin illuminating light

We observe finally the novel possibility of using so-called lin \perp lin illuminating light which is essentially *achiral*, rather than illuminating light comprised of a single circularly polarised plane wave, to extract information about the chirality of the molecules through I . We associate with this illuminating light a quantity analogous to $\Delta^{(0)}(\hat{\mathbf{x}})$ that is impervious to spurious contributions attributable to circular dichroism whilst being of a different form.

Consider then a superposition of two linearly polarised plane waves of equal amplitude E_0 , the first of which is polarised along the x axis and propagates in the $+z$ direction whilst the second is polarised along the y axis and propagates in the $-z$ direction as

$$\begin{aligned}\tilde{\mathbf{E}}^{(3)} &= E_0 i\hat{\mathbf{x}} \exp(i|\mathbf{k}|z) - E_0 i\hat{\mathbf{y}} \exp(-i|\mathbf{k}|z), \\ \tilde{\mathbf{B}}^{(3)} &= E_0 i\hat{\mathbf{y}} \exp(i|\mathbf{k}|z)/c - E_0 i\hat{\mathbf{x}} \exp(-i|\mathbf{k}|z)/c.\end{aligned}\tag{5.74}$$

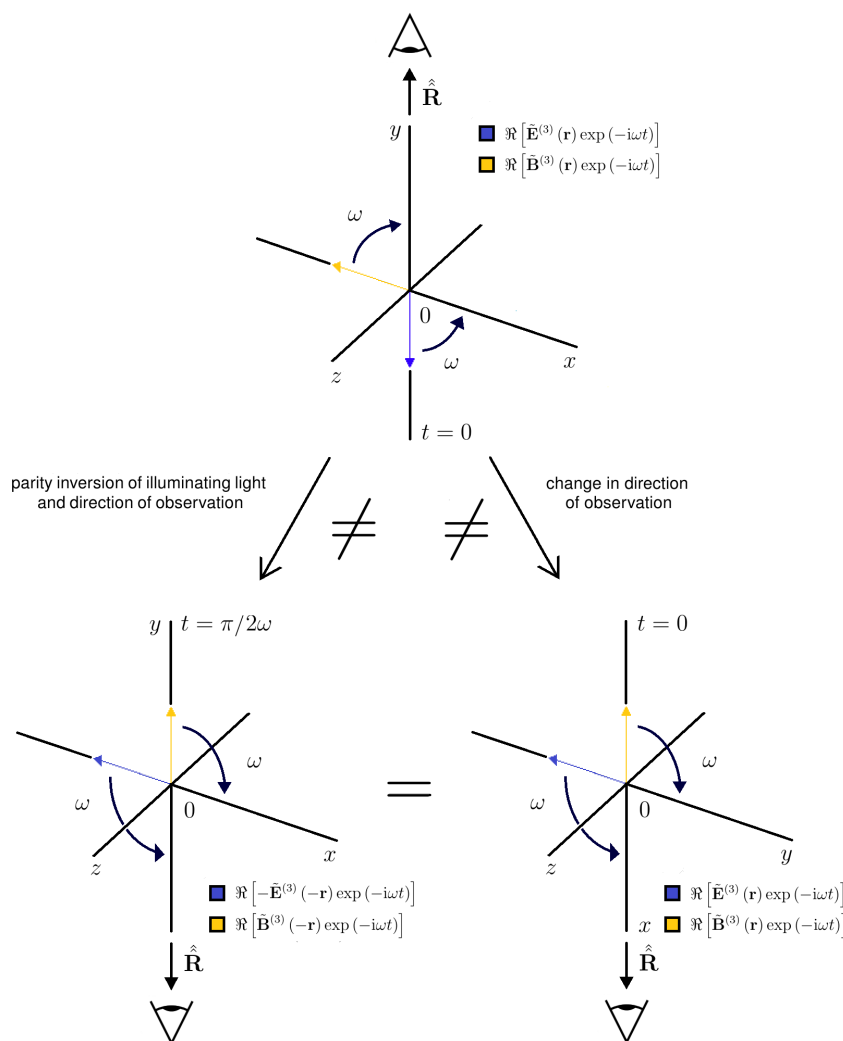


Figure 5.8: A parity inversion of the lin \perp lin illuminating light and the direction of observation $\hat{\mathbf{R}} = \hat{\mathbf{y}}$ through the origin $\mathbf{r} = 0$ can be mimicked in the $z = 0$ plane by leaving the light unaltered and changing the direction of observation from $\hat{\mathbf{R}} = \hat{\mathbf{y}}$ to $\hat{\mathbf{R}} = \hat{\mathbf{x}}$.

It should be noted that we only have one form of illuminating light here, in contrast to examples zero, one and two where there were two forms of illuminating light which we distinguished using plus and minus signs. It is essentially the same as the light examined in §3.3.8. In the $z = 0$ plane, \mathbf{E} and \mathbf{B} rotate in opposite directions which is, by itself, an essentially achiral configuration. The combination of \mathbf{E} , \mathbf{B} and $\hat{\mathbf{R}}$, however, is chiral in general. In particular, a parity inversion of the illuminating light and the direction of observation $\hat{\mathbf{R}} = \hat{\mathbf{y}}$ through $\mathbf{r} = 0$ yields a new configuration not superposable upon the old. An essentially equivalent transformation is invoked, however, by leaving the illuminating light unaltered and changing the direction of observation from $\hat{\mathbf{R}} = \hat{\mathbf{y}}$ to $\hat{\mathbf{R}} = \hat{\mathbf{x}}$. This is depicted in figure 5.8.

Let us suppose then that the molecules are distributed homogeneously in the $z = 0$ plane about

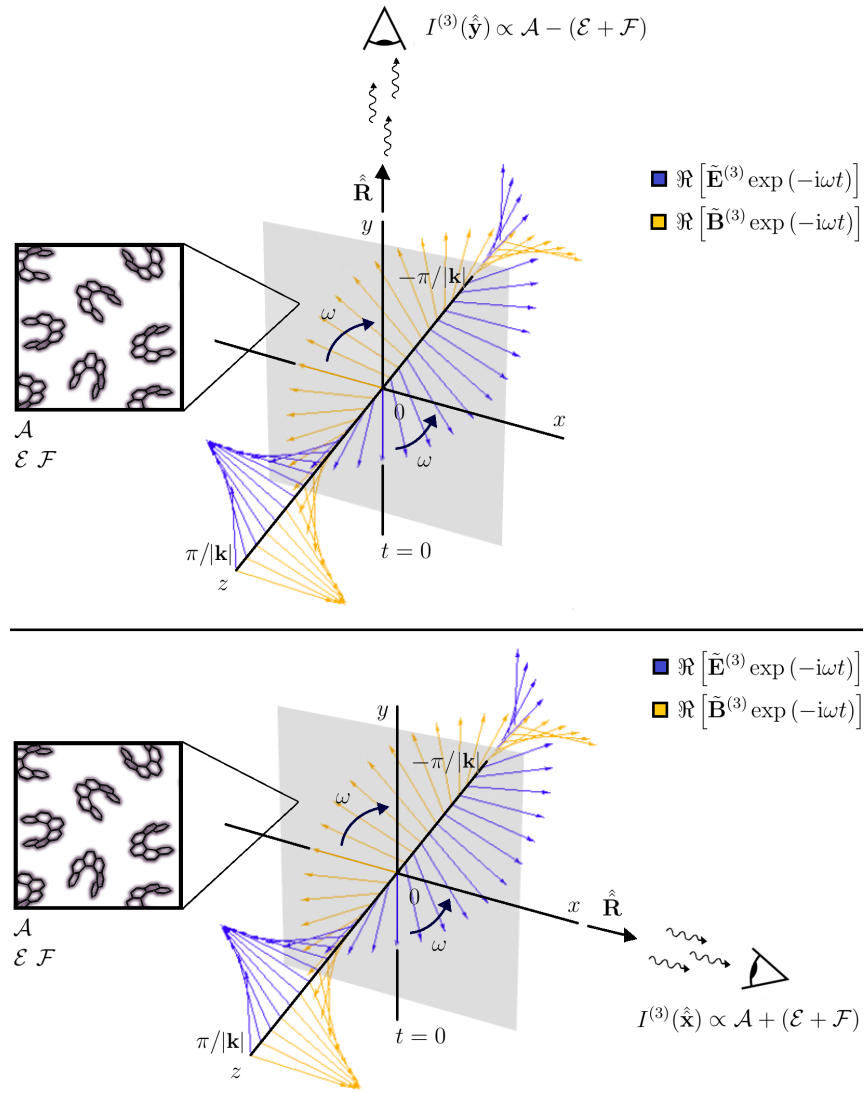


Figure 5.9: $\text{Lin} \perp \text{lin}$ illuminating light, which is by itself essentially achiral, can be employed to probe the chirality of the molecules by making explicit use of the degree of freedom that is the direction in which the intensity of scattered light is observed.

$\mathbf{r} = 0$. We find that

$$\begin{aligned} I^{(3)}(\hat{\mathbf{x}}) &\approx \frac{\epsilon_0 N K E_0^2}{|\mathbf{R}|^2} [\mathcal{A} + (\mathcal{E} + \mathcal{F})], \\ I^{(3)}(\hat{\mathbf{y}}) &\approx \frac{\epsilon_0 N K E_0^2}{|\mathbf{R}|^2} [\mathcal{A} - (\mathcal{E} + \mathcal{F})]. \end{aligned} \quad (5.75)$$

Evidently, information about the chirality of the molecules can be extracted simply by contrasting $I^{(3)}(\hat{\mathbf{x}})$ and $I^{(3)}(\hat{\mathbf{y}})$. This is of course possible owing to the equivalence described above.

We quantify this phenomenon through a generalised intensity difference $\Upsilon^{(3)}$ defined as

$$\begin{aligned}\Upsilon^{(3)} &= \frac{I^{(3)}(\hat{\mathbf{y}}) - I^{(3)}(\hat{\mathbf{x}})}{I^{(3)}(\hat{\mathbf{y}}) + I^{(3)}(\hat{\mathbf{x}})} \\ &\approx -\frac{\mathcal{E} + \mathcal{F}}{\mathcal{A}} \\ &= \frac{2(45aG' + \beta_G^2 - \beta_A^2)}{c(45a^2 + 13\beta^2)},\end{aligned}\tag{5.76}$$

which has equal magnitudes but opposite signs for opposite molecular enantiomers. This $\Upsilon^{(3)}$ is of a different character, of course, to $\Delta^{(0)}$, $\chi^{(1)}$ and $\Lambda^{(2)}$ as it is dependent upon scattered intensities associated with one form of illuminating light rather than two. It offers somewhat different information about the chirality of the molecules than $\Delta^{(0)}(\hat{\mathbf{x}})$: the contributions made by β_G^2 and β_A^2 to $\Upsilon^{(3)}$ are of opposite sign to those in $\Delta^{(0)}(\hat{\mathbf{x}})$ and the former is 13 times smaller. Although we have assumed the illuminating light to be off resonance, there will always exist in reality some absorption of the illuminating light by the molecules. Owing to circular dichroism, $\Delta^{(0)}(\hat{\mathbf{x}})$, $\chi^{(1)}$ and $\Lambda^{(2)}$ will therefore suffer from spurious contributions attributable not to light scattering but rather, to luminescence. By its very nature, $\Upsilon^{(3)}$, however, is impervious to such contributions. Indeed, $\text{lin} \perp \text{lin}$ illuminating light will be absorbed at the same rate by opposite molecular enantiomers, as it is essentially achiral.

Thus concludes our present consideration of optical activity in the scattering of light. Our proposed techniques require that the scattering molecules be confined to a plane, in which case their number and hence, the scattered intensity, is necessarily reduced relative to that attainable in a fully homogeneous sample. It is unclear at present whether this limitation can be overcome simply. In experiment, such confinement might be realised simply by depositing the molecules onto a surface [168]. Of course, additional effects associated with the surface, such as reflection and refraction of the illuminating light and molecular orientation [169], would then have to be considered with care. For our two-plane-wave examples, we restricted our attention to right-angled observation which is particularly well suited to experiment as it ‘avoids’ the illuminating light as much as possible. Nevertheless, more information about the chirality of the molecules may be extracted by exploring other scattering geometries, as has been suggested for illuminating light comprised of single circularly polarised plane waves [156]. Our approach has been centred upon the unanalysed scattered intensity as this is, perhaps, the most readily measurable property of the scattered light. The polarisation properties of the scattered light remain to be explored, however, and may yield additional possibilities. Finally, we highlight the fact that analogous approaches to those undertaken in the present section can be pursued for other manifestations of optical activity in light scattering. These are tasks for future research.

5.4 Discriminatory optical force for chiral molecules

It is well established that chiral molecules can exert discriminatory forces upon *each other* [12, 170, 171]. In recent years, interest has been expressed regarding the possibility of using *light*, such as that produced by a laser, to exert a force of discriminatory character upon a *single* chiral molecule

[172–176]. The present section is concerned with this possibility. We observe that the centre-of-mass motion of a chiral molecule is, under appropriate circumstances, sensitive to gradients in the helicity of an optical field and that the force associated with these gradients points in *opposite* directions for the opposite enantiomers of the molecule. We present a simple optical field for which this phenomenon is isolated and propose applications. Our approach differs, it seems, from others that have been presented in the literature [172–176] in that we make no critical assumptions regarding the energy-level structure of the molecule but rather, rely upon the sign of a certain molecular polarisability. Our work is, therefore, relevant for many types of molecule and our proposed applications may be realisable using currently existing technology.

5.4.1 Force exerted by light upon a chiral molecule

Consider a chiral molecule located at position $\mathbf{R} = X\hat{\mathbf{x}} + Y\hat{\mathbf{y}} + Z\hat{\mathbf{z}}$. We assume an absence of applied static electric and magnetic fields but suppose, however, that the molecule is illuminated by weak, monochromatic, far off-resonance light of angular frequency $\omega = c|\mathbf{k}|$, the length scale $2\pi/|\mathbf{k}|$ associated with which is larger than the molecule. The electric field \mathbf{E} and magnetic flux density \mathbf{B} comprising the light are described by (1.75)-(1.80): we regard the light as being an externally imposed influence acting upon the molecule to which it is introduced in an adiabatic manner. We imagine the molecule to be rotating and perhaps vibrating somewhat such that we can ignore molecular alignment: we imagine the molecule to be ‘tumbling’ freely in the optical field. In reality, the molecule might be a constituent of a hot effusive molecular beam and the light might originate from a near-infrared laser.

During the course of their interactions the light and the molecule will, in general, exchange linear momentum, giving rise to an optical force which governs the centre-of-mass motion of the molecule [28, 177]. Well-established optical activity phenomena [12, 25, 27, 143] suggest to us the possibility that the opposite enantiomers of the molecule will, in general, exchange linear momentum with light of chiral character at different rates, thus experiencing different optical forces. We now demonstrate this to be the case.

We neglect the forces experienced by the particles comprising the molecule due to their own electromagnetic fields, which give rise, in particular, to radiation reaction effects [2, 3, 11]. Moreover, we approximate the true electromagnetic interactions between the particles by non-retarded Coulomb interactions [11], the forces associated with which cancel for any given pair of particles. Thus, the net electromagnetic force $\mathbf{F} = \mathbf{F}(t)$ experienced by the molecule derives solely from the Lorentz

forces exerted upon the individual particles by the optical field as

$$\begin{aligned}
\mathbf{F} &= \sum_{n=1}^N q_n [\mathbf{E}(\mathbf{r}_n, t) + \dot{\mathbf{r}}_n \times \mathbf{B}(\mathbf{r}_n, t)] \\
&= \iiint_{\infty} (\rho \mathbf{E} + \mathbf{J} \times \mathbf{B}) d^3\mathbf{r} \\
&= \iiint_{\infty} [(-\nabla \cdot \mathbf{P}) \mathbf{E} + (\dot{\mathbf{P}} + \nabla \times \mathbf{M}) \times \mathbf{B}] d^3\mathbf{r} \\
&= \iiint_{\infty} [P_{(a)} \nabla E_{(a)} + M_{(a)} \nabla B_{(a)}] d^3\mathbf{r} + \frac{d}{dt} \iiint_{\infty} \mathbf{P} \times \mathbf{B} d^3\mathbf{r}. \tag{5.77}
\end{aligned}$$

Making use now of the results presented in §1.4, we find that the cycle-averaged, rotationally-averaged form $\langle \bar{\mathbf{F}} \rangle$ of \mathbf{F} is conservative, being comprised of two distinct pieces as

$$\langle \bar{\mathbf{F}} \rangle = -\nabla U_w(\mathbf{R}) - \nabla U_h(\mathbf{R}), \tag{5.78}$$

with the potential energies $U_w = U_w(\mathbf{r})$ and $U_h = U_h(\mathbf{r})$ as defined below. Note that in obtaining the result seen in (5.78), we supposed \mathbf{R} to be fixed. In what follows, however, we employ this result to describe scenarios in which \mathbf{R} may be changing with t . In doing so, we neglect certain phenomena attributable directly to the centre-of-mass motion of the molecule (Röntgen current, Doppler shifts etc [12, 177]), the effects of which will be small for realistic molecular speeds.

U_w is the familiar ‘dipole’ potential energy [177, 178]:

$$U_w = -\alpha \bar{w}_E / \epsilon_0, \tag{5.79}$$

with $3\alpha = \alpha_{(aa)}(\omega)$. Except for a factor of twice the speed of light c , \bar{w}_E is often referred to loosely as the ‘intensity’ of an optical field, although this nomenclature is not appropriate in general. It seems natural that the trace 3α should appear in connection with the electric energy density w_E . The former is a time-even rotational scalar associated with the interference of electric-dipole transition moments within a molecule [25] whilst the latter is a time-even rotational scalar field that is also of apparent electric character [2]. For ω far off-resonance, 3α may be well-approximated by its static value, which is usually positive [25, 179]. In general, w_E is also positive although it may, of course, vanish at certain points in space at certain times. U_w thus *attracts* the molecule towards those regions in the optical field where the cycle-averaged electric energy density \bar{w}_E is maximum. The employment of the dipole potential energy to manipulate molecules has been pursued in a wealth of theoretical [179–195] and experimental [196–213] contexts.

U_h is

$$U_h = \omega G' \bar{h} / \epsilon_0 c, \tag{5.80}$$

with $3G' = G'_{(aa)}(\omega)$. It seems natural that the trace $3G'$ should appear in connection with the helicity density h . The former is a time-even rotational pseudoscalar associated with the mutual interference

of electric-dipole and magnetic-dipole transition moments within a molecule [25] whilst the latter is a time-even rotational pseudoscalar field that embodies the electric-magnetic symmetry inherent to freely-propagating light. Moreover, such transformation properties are the hallmarks of true chirality [25, 141, 142, 214] and indeed, $3G'$ possesses equal magnitudes but opposite *signs* for the opposite enantiomers of a chiral molecule [12, 27, 171] whilst the helicity \mathcal{H} itself possesses equal magnitudes but opposite signs for the enantiomorphs of an optical field. Thus, the force $-\nabla U_h(\mathbf{R})$ associated with U_h is entirely discriminatory, pointing in opposite directions for the opposite enantiomers of the molecule: U_h attracts the enantiomer for which $3G' > 0$ towards those regions in the optical field where the cycle-averaged value helicity density \bar{h} is minimum whilst the opposite enantiomer, with $3G' < 0$, is instead attracted to those regions in the optical field where \bar{h} is maximum. This is, in essence, our main result.

At the time of publishing the original research described in the present section [150, 151], expressions for the optical force experienced by a small isotropic chiral dipole of unspecified constitution, as induced by monochromatic light, had been reported independently elsewhere [215–217]. In these expressions, a contribution can be identified that coincides with the discriminatory optical force $-\nabla U_h(\mathbf{R})$. This is natural, of course, as we have treated the molecule much like such a dipole. Applications for the discriminatory optical force additional to those proposed below have since been proposed elsewhere [218].

Although the derivation given in the present section and indeed, the concept of a force, is classical in nature, the forms of U_w and U_h can also be justified by an appropriate calculation in the quantum domain. Indeed, it will be noticed that they coincide with the energy shifts discussed in §5.2.4. Thus, our discriminatory optical force and optical rotation are, in fact, different manifestations of the same interaction!

5.4.2 Isolating the discriminatory optical force

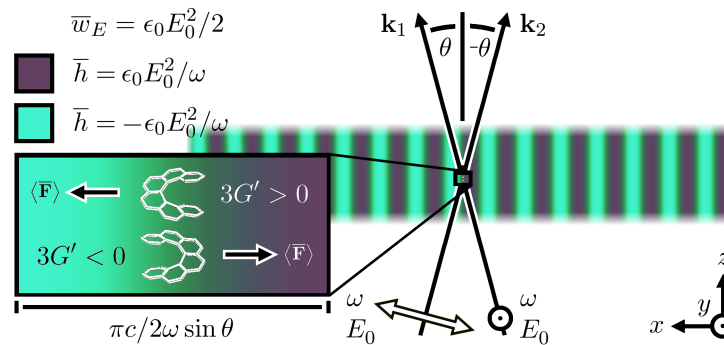


Figure 5.10: Light possessing helicity fringes can give rise to a cycle averaged, rotationally averaged optical force $\langle \mathbf{F} \rangle$ that is, in general, non-vanishing and is purely discriminatory; pointing in opposite directions for the opposite enantiomers of a chiral molecule, as illustrated for the enantiomers of hexahelicene.

A simple estimate reveals that the ratio $|c\alpha/G'|$ is typically of the order of 10^3 - 10^5 [12, 25, 170] and so it may appear that $-\nabla U_w(\mathbf{R})$ overwhelms $-\nabla U_h(\mathbf{R})$. This need *not* be the case, however:

we can, in fact, *eliminate* the former so that $\langle \bar{\mathbf{F}} \rangle$ is entirely discriminatory in turn, by constructing the optical field such that \bar{w}_E is homogeneous (and, therefore, $\nabla \bar{w}_E(\mathbf{R}) = 0$) whilst \bar{h} is not (and $\nabla \bar{h}(\mathbf{R}) \neq 0$).

To demonstrate this, let us consider the optical field constructed by superposing two linearly polarised plane waves of equal amplitude E_0 and angular frequency ω , propagating such that their wavevectors lie in the x - z plane making angles of $\pm\theta$ ($\theta > 0$) with the $+z$ axis. We take the polarisations of the $\pm\theta$ waves to lie in the x - z plane and parallel to the y axis respectively. Explicitly

$$\begin{aligned} \tilde{\mathbf{E}} &= E_0(\hat{\mathbf{x}} \cos \theta - \hat{\mathbf{z}} \sin \theta) \exp[i|\mathbf{k}|(z \cos \theta + x \sin \theta)] \\ &\quad + E_0 \hat{\mathbf{y}} \exp[i|\mathbf{k}|(z \cos \theta - x \sin \theta)], \end{aligned} \quad (5.81)$$

$$\begin{aligned} \tilde{\mathbf{B}} &= E_0 \hat{\mathbf{y}} \exp[i|\mathbf{k}|(z \cos \theta + x \sin \theta)]/c \\ &\quad + E_0(-\hat{\mathbf{x}} \cos \theta - \hat{\mathbf{z}} \sin \theta) \exp[i|\mathbf{k}|(z \cos \theta - x \sin \theta)]/c. \end{aligned} \quad (5.82)$$

This optical field is identical to that examined in §3.3.8, but with the angle $\vartheta = \pi/2$ here. As will be recalled, it sports *helicity fringes* attributable to quasi-interference. We find that

$$U_w = -\alpha E_0^2/2, \quad (5.83)$$

$$U_h = -G' E_0^2 \cos^2 \theta \sin(\kappa x)/c, \quad (5.84)$$

with $\kappa = 2\omega \sin \theta/c$ a wavenumber. Thus,

$$\langle \bar{\mathbf{F}} \rangle = \kappa G' E_0^2 \cos^2 \theta \cos(\kappa X) \hat{\mathbf{x}}/c, \quad (5.85)$$

which is non vanishing, in general, and points in opposite directions for the opposite enantiomers of the molecule, by virtue of the opposite signs of $3G'$, as claimed. This is depicted in figure 5.10.

It is possible, of course, to conceive of many other optical fields for which \bar{w}_E is homogeneous whilst \bar{h} is not. We emphasise that $\langle \bar{\mathbf{F}} \rangle$ is entirely discriminatory in *all* such cases. The simple examples of which we are aware are obtained, as above, from various superpositions of waves that possess linear and orthogonal polarisations [53, 79].

5.4.3 Newtonian molecular optics

The field of Newtonian molecular optics is concerned with the manipulation of the centre-of-mass motion of a molecule in a regime where the motion can be viewed classically [177], as we have presumed to be the case so far. The *dipole* optical force has been utilised successfully in this regime in a multitude of experiments [196, 197, 199, 201, 202, 204–207, 211–213]. It seems natural, therefore, to investigate the novel possibilities offered for our molecule in the regime of Newtonian molecular optics by the *discriminatory* optical force.

Chiral Stern-Gerlach deflector

The use of an optical field akin to the one presented in §5.4.2 to *deflect* the centre-of-mass trajectory of the molecule in a discriminatory manner with a single helicity fringe, say, presents itself as one possibility: see figure 5.11. In homage to a traditional Stern-Gerlach deflector [219], we refer to this device as a ‘chiral Stern-Gerlach deflector’.

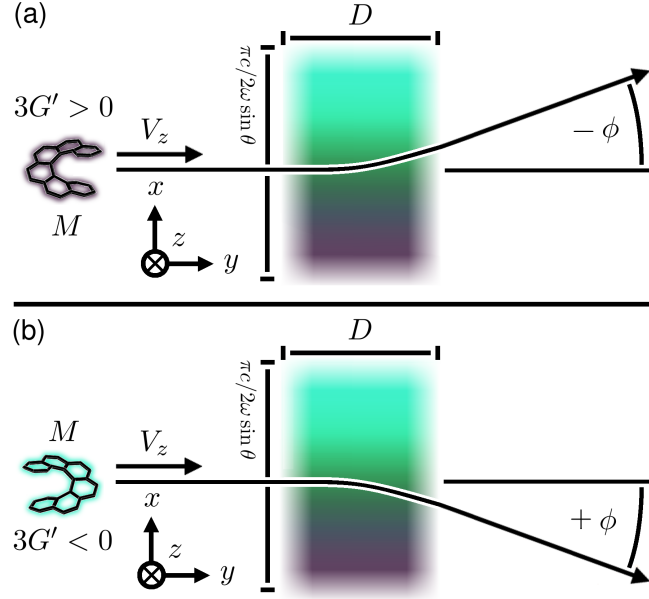


Figure 5.11: The principle of operation of the chiral Stern-Gerlach deflector, depicted here for the opposite enantiomers of hexahelicene. (a) A single helicity fringe deflects the left-handed enantiomer to the left. (b) The same fringe deflects the right-handed enantiomer to the right.

Let us now perform a simple estimate to gauge the feasibility of the chiral Stern-Gerlach deflector. We suppose that the molecule, of observable rest mass M , resides, at $t = 0$, at the origin $\mathbf{r} = 0$ of the optical field presented in §5.4.2, moving in the $+z$ direction with speed V_z . We suppose, moreover, that its subsequent centre-of-mass motion is governed by Newton’s second law and $\langle \mathbf{F} \rangle$ as seen in (5.85). Considering an interaction time $0 < t \ll \sqrt{Mc/\kappa^2|G'|E_0^2}$ such that the molecule does not reach its nearest helicity trough or peak and $|X(t)| \ll \pi/2\kappa$, we deduce that its angular deflection $\phi = \phi(t)$, as measured with respect to the $+z$ axis, is

$$\phi \approx -t\kappa G' E_0^2 / MV_z c, \quad (5.86)$$

to first order in ϕ , as we presume that $\phi \ll 1$. We consider $\omega = 2 \times 10^{15} \text{ s}^{-1}$ which corresponds to a free-space wavelength of $2\pi c/\omega = 1 \times 10^{-6} \text{ m}$. This lies in the near infrared to which many molecules are indeed essentially transparent [196, 197, 199, 201, 202, 204–207, 211, 213]. We choose $\theta = 5 \times 10^{-2}$ which yields helicity fringes of wavelength $2\pi/\kappa = \pi c/\omega \sin \theta = 1 \times 10^{-5} \text{ m}$, which is also in line with experimental demonstrations [80, 81]. For the sake of concreteness, we consider hexahelicene, a chiral molecule with $M = 5 \times 10^{-25} \text{ kg}$ [25, 34, 35]. Using an empirical result obtained from a measurement of specific rotation [25, 34, 35], together with an appropriate theoretical angular frequency scaling [25, 220], we estimate that $3G' = \pm 1 \times 10^{-34} \text{ m kg}^{-1} \text{ s}^3 \text{ A}^2$, where the plus and minus signs refer to the left- and right-handed enantiomers of the molecule.

We consider $E_0 = 6 \times 10^8 \text{ m kg s}^{-3} \text{ A}^{-1}$ which corresponds to a notional intensity of $\epsilon_0 c E_0^2 = 1 \times 10^{15} \text{ kg s}^{-3}$. The latter is approximately one order of magnitude *smaller* than that typically employed [196, 197, 199, 202, 204–207, 211, 213] which may help to reduce the possible effects of polarisation dependent alignment [211, 212] that threaten to complicate our picture and also allows us, we assume, to consider $t = 1 \times 10^{-6} \text{ s}$ which is approximately two orders of magnitude larger than the usual interaction time [196, 197, 199, 201, 202, 204–207, 211, 213]: the probabilities of certain processes such as multi-photon ionisation that promise to damage the molecule, thus limiting the maximum interaction time, scale in a highly non-linear fashion with intensity [196, 197]. We take $V_z = 1 \times 10^2 \text{ m s}^{-1}$, as may be obtained with a velocity selector⁵ [221], and identify a notional longitudinal width $D = V_z t = 1 \times 10^{-4} \text{ m}$ of the optical field. Using these values in (5.86), we find that

$$\phi = \pm 5 \times 10^{-4}. \quad (5.87)$$

Even for our optimistic estimate, ϕ is rather ‘small’. We believe nevertheless that such deflections are detectable, perhaps using the methods that have already been employed in analogous experiments centred upon the dipole optical force, namely the ionisation of deflected molecules using an intense laser beam and their subsequent detection using a microchannel plate detector in a suitable geometry [196, 197, 199, 201, 202, 204, 211]. The utilisation of these methods in particular to map modifications of molecular trajectories attributable to the dipole optical force has been well-demonstrated [199, 202].

A chiral Stern-Gerlach deflector could be employed as a robust means of spatially separating the enantiomers of a chiral molecule for further applications. It is possible that this might find practical use in pharmaceutical research, for example, where efficient methods of chiral resolution may not be known for a newly-synthesised chiral molecule [143] and yet, it is of vital importance to work with samples of a known enantiomeric purity *a priori*, as is exemplified by methamphetamine and other drugs besides. In addition, a chiral Stern-Gerlach deflector might be utilised to measure the magnitude and sign of $3G'$ supported by a molecule, by examining the magnitude and direction of the associated deflection. It could even be used as a means of determining the enantiomeric purity of a sample of chiral molecules by passing some of them through the device and comparing the numbers deflected to the left and to the right. Closely related devices have been proposed theoretically elsewhere [172, 174–176], albeit making use of seemingly different mechanisms.

It is possible, of course, to conceive of other novel possibilities offered for chiral molecules in the regime of Newtonian molecular optics by the dipole optical force. At present, however, we turn our attention to a more delicate but *sensitive* regime, namely that of de Broglie molecular optics.

5.4.4 de Broglie molecular optics

Ultimately, the centre-of-mass motion of a molecule is governed by the laws of quantum mechanics and should most accurately be viewed in terms of de Broglie waves [28, 177]. The manipulation

⁵It is important that the internal temperature of the molecule be sufficiently high so as to justify our use of rotational averaging: an effusive source of temperature $T = 1 \times 10^3 \text{ K}$, say, may suffice.

of these waves comprises the field of de Broglie molecular optics, in which there exist possibilities including the performance of remarkably high precision measurements [28, 177] that cannot be understood in terms of Newtonian trajectories [28, 177]. Indeed, the picture presented in Newtonian molecular optics is but an approximation to the more fundamental one presented in de Broglie molecular optics, much as the picture presented in geometrical optics is but an approximation to the more fundamental one presented in the wave theory of light [27]. The *dipole* potential energy has been utilised successfully in the regime of de Broglie molecular optics in various experiments [203, 208–210, 222] and it seems natural, therefore, to enquire as to the novel possibilities offered for our molecule by the *discriminatory* potential energy. Thus, let us now assume coherent quantum-mechanical evolution of the centre-of-mass motion of the molecule.

Chiral diffraction grating

We recognise, for example, the possibility of using an optical field akin to the one presented in §5.4.2 to diffract the de Broglie waves associated with the centre-of-mass motion of the molecule, by passing them through a thin sheet of helicity fringes as illustrated in figure 5.12(a). The sensitivity of the de Broglie waves to the helicity fringes and thus, the diffraction, is attributable to the molecule being chiral ($3G' \neq 0$): the de Broglie waves associated with the centre-of-mass motion of a similar achiral molecule are instead insensitive to the helicity fringes (as $3G' = 0$ [12, 27, 171]) and, therefore, no diffraction results, as illustrated in figure 5.12(b). We refer to this device accordingly as a ‘chiral diffraction grating’.

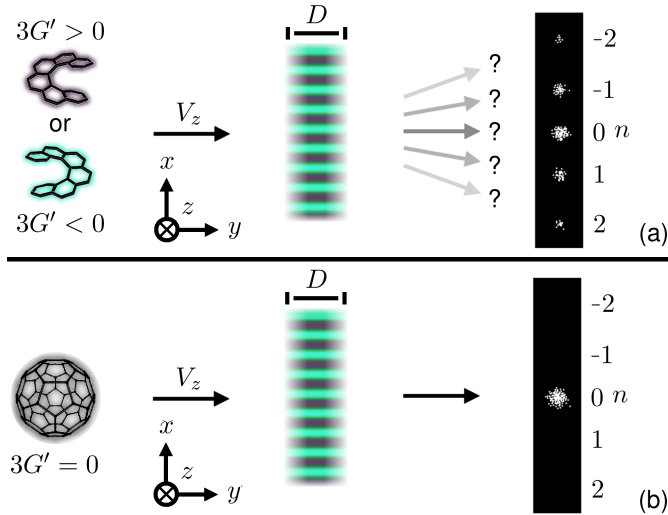


Figure 5.12: The principle of operation of the chiral diffraction grating. (a) A chiral molecule such as hexahelicene is diffracted by a collection of helicity fringes. (b) An achiral molecule such as buckminsterfullerene (C_{60}) does not ‘sense’ these fringes and hence, is not diffracted.

Let us now consider the results of some simple calculations pertaining to the chiral diffraction grating. We suppose that the molecule resides in the optical field presented in section 5.4.2 and describe it as a point particle behaving in accord with the Schrödinger equation under the influence of U_w and U_h as seen in (5.83) and (5.84). We suppose, moreover, that the molecule occupies, at $t = 0$, a linear momentum eigenstate with eigenvalue $MV_z\hat{z}$. Considering an interaction time $0 < t \ll 2Mc^2/\hbar\omega^2$

significantly shorter than the inverse of the single-photon recoil angular frequency, say, we employ the Raman-Nath approximation and find, following a slight variant of a standard calculation [223], that the molecule evolves into a superposition of linear momentum eigenstates with eigenvalues $n\hbar\kappa\hat{\mathbf{x}} + MV_z\hat{\mathbf{z}}$, where $n \in \{0, \pm 1, \dots\}$ and the probabilities associated with these eigenvalues are

$$P_n = J_n^2(tG'E_0^2 \cos^2 \theta / \hbar c). \quad (5.88)$$

In reality, we may associate t with a notional longitudinal width D of the optical field as $t = D/V_z$. The Raman-Nath approximation then corresponds to a ‘thin’ [177, 223] chiral diffraction grating and the relative intensities of the diffraction orders ($n = 0, \pm 1, \pm 2, \dots$) observable in the far field [203, 222] are governed by the probabilities P_n . This conclusion can also be reached, of course, by calculating a Fraunhofer diffraction integral [224]. It will be noticed that the P_n depend upon the magnitude of $3G'$ but not the sign. They are, therefore, equal for the opposite enantiomers of the molecule. Consider now, as in §5.4.3, $\omega = 2 \times 10^{15} \text{ s}^{-1}$ and hexahelicene, for which $M = 5 \times 10^{-25} \text{ kg}$ and we estimate $3G' = \pm 1 \times 10^{-34} \text{ m kg}^{-1} \text{ s}^3 \text{ A}^2$, as will be recalled. We choose $\theta = 5 \times 10^{-1}$ here which yields helicity fringes of wavelength $2\pi/\kappa = \pi c/\omega \sin \theta = 1 \times 10^{-6} \text{ m}$. In line with an analogous experiment in which the diffraction of fullerenes due to their interaction with a traditional optical standing wave was observed, we take $V_z = 1 \times 10^2 \text{ m s}^{-1}$ and $D = 5 \times 10^{-5} \text{ m}$ [203, 222], corresponding to $t = D/V_z = 5 \times 10^{-7} \text{ s}$. With $3G'$, θ and t fixed, the P_n are found to depend upon E_0 and hence, $\epsilon_0 c E_0^2$ in a highly sensitive manner, as seen in figure 5.13. In choosing these values, we have also accounted for effects not included explicitly in our analysis so as to ensure the possibility of an experimental demonstration: the helicity fringes are unlikely to be resolved via quasi-blackbody radiation by a velocity-selected effusive molecular source of temperature $T = 1 \times 10^3 \text{ K}$, say, whilst this temperature ensures the validity of our use of rotational averaging [225, 226]; the diffraction orders should be separated by $1 \times 10^{-5} \text{ m}$ when observed 1 m away from the chiral diffraction grating and could be recorded, therefore, using the same methods that have already been employed in molecular diffraction experiments centred upon the dipole potential energy, namely the ionisation of diffracted molecules using an intense laser beam, translated across the diffraction pattern, and their subsequent detection using an electron multiplier [203]; the highest notional intensity considered of $\epsilon_0 c E_0^2 = 3 \times 10^{13} \text{ kg s}^{-3}$ represents an upper limit beyond which the probability of the molecule absorbing at least one photon from the optical grating approaches unity, as extrapolated from hexahelicene’s measured visible absorption spectrum [226–228].

The chiral diffraction grating and its associated diffraction patterns are also remarkably sensitive to the chiral geometry of the molecule. To illustrate this, we now employ an analytical expression for hexahelicene’s trace $3G'$, obtained elsewhere using a dynamic coupling model [25, 229, 230], and fix $E_0 = 1 \times 10^8 \text{ m kg s}^{-3} \text{ A}^{-1}$ so that $\epsilon_0 c E_0^2 = 3 \times 10^{13} \text{ kg s}^{-3}$. We vary the normalised pitch $-1 \leq \gamma \leq 1$ of the molecule in a hypothetical manner, however, and examine the corresponding changes in the P_n . As the P_n are identical for the opposite enantiomers of the molecule, we need only consider the magnitude of γ . The limiting values $|\gamma| = 1$ and $|\gamma| = 0$ correspond to the usual helical shape adopted by hexahelicene and to a ‘flattened’ version of the molecule which is achiral. Thus, for $|\gamma| = 1$ our chiral diffraction grating gives rise to the diffraction pattern expected of hexahe-

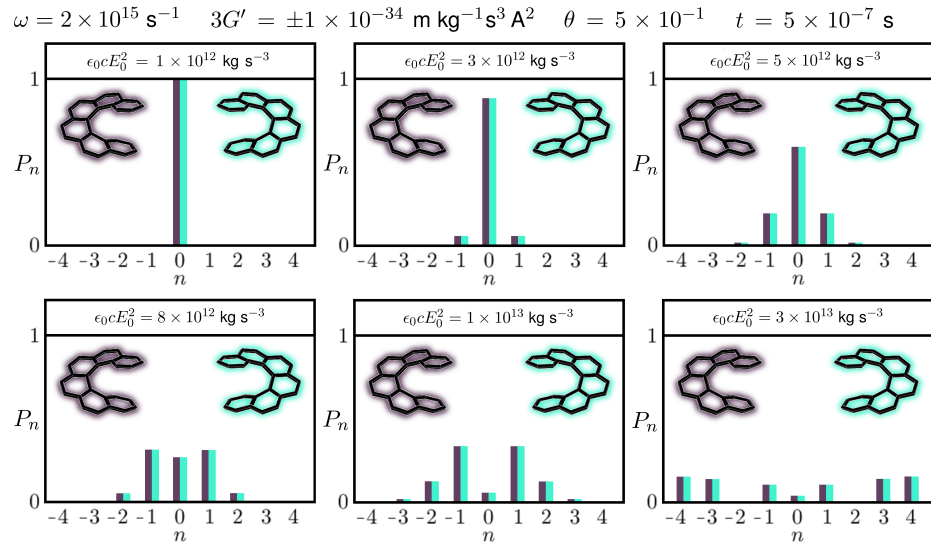


Figure 5.13: Plots of the diffraction probabilities P_n , depicting their variation with the notional intensity $\epsilon_0 c E_0^2$ for hexahelicene.

licene in reality⁶ whereas for $|\gamma| = 0$, no diffraction pattern is found. Between these limiting cases, the P_n vary drastically in responses to ‘small’ changes in $|\gamma|$ as seen in figure 5.14.

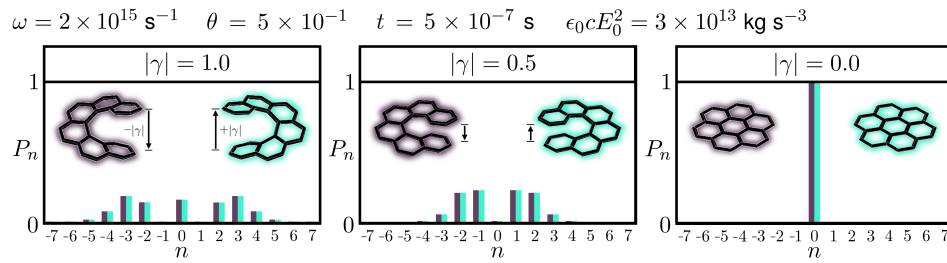


Figure 5.14: Plots of the diffraction probabilities P_n , depicting their (hypothetical) variation with the magnitude of the normalised pitch γ of hexahelicene.

We highlight here once more that the P_n are equal for the opposite enantiomers of the molecule. Consequently, the diffraction patterns produced by a chiral diffraction grating in practice would be *insensitive* to the enantiomeric purity of the source from which the molecules derive and a racemic mixture in particular, which does not exhibit any traditional manifestations of optical activity (optical rotation, circular dichroism, differential scattering), would give rise to the *same* non-trivial diffraction patterns as it would if it were enantiopure! The chiral diffraction grating should be viewed, therefore, as something of a chirality *detector*, rather than a chirality *discriminator*: the very existence of diffraction indicates that $|3G'| \neq 0$ and hence that a molecule is chiral. By examining the diffraction patterns it produces, a chiral diffraction grating could be employed to measure, to high precision, the value of $|3G'|$ supported by a molecule. Its insensitivity to the sign of $3G'$ lends the chiral diffraction grating to more exotic applications besides, for example the detection of, and measurement of the concentration of, racemic distributions of chiral impurities in otherwise achiral samples.

⁶The difference in appearance of the last panel of figure 5.13 and the first panel of figure 5.14 is due to the fact that they were derived from empirical and theoretical values of $3G'$ that themselves differ slightly.

Discriminatory chiral diffraction grating

We can incorporate the discriminatory character of the chiral Stern-Gerlach deflector into the chiral diffraction grating, whilst retaining the sensitivity of the latter, by placing a thin mechanical transmission grating in front of the helicity fringes such that those regions for which $(\nabla H)_x > 0$ are obscured, as illustrated in figure 5.15. We determine the modified diffraction probabilities P'_n by calculating a Fraunhofer diffracton integral [231] whilst neglecting van der Waals forces associated with the mechanical grating. The P'_n now discriminate between the enantiomers of the molecule, being sensitive to both the magnitude and sign of $3G'$, as seen in figure 5.16. We refer to our new device accordingly as a ‘discriminatory chiral diffraction grating’.

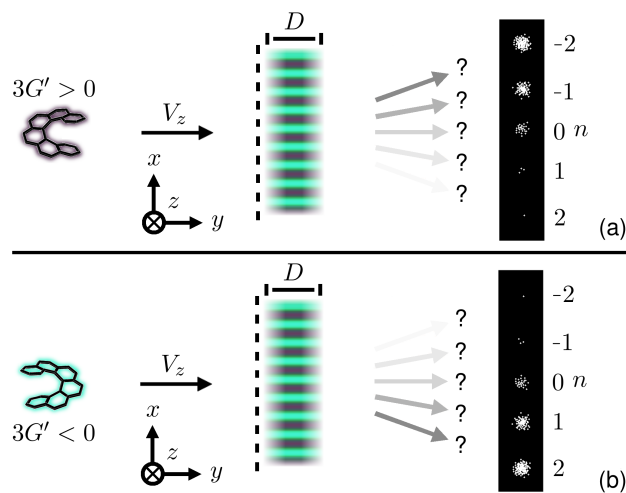


Figure 5.15: The discriminatory chiral diffraction grating: a composite of a thin mechanical transmission grating and a thin sheet of helicity fringes, gives rise to diffraction patterns that discriminate between the enantiomers a chiral molecule as illustrated for the left- (a) and right-handed (b) enantiomers of hexahelicene.

A discriminatory chiral diffraction grating could be employed as a means of spatially separating the enantiomers of a chiral molecule for further applications. In this context we might regard it as a chiral beam splitter for de Broglie waves. In addition, it might be utilised to measure, to high precision, the magnitude and sign of $3G'$ supported by a molecule by examining the form of the associated diffraction pattern. If $|3G'|$ in particular is already known for a type of chiral molecule, our discriminatory chiral diffraction grating could be employed instead to measure, simply and to high precision, the enantiomeric excess $ee = (n_L - n_R)/(n_L + n_R)$ of a sample, where $n_L + n_R = n \gg 1$ is the total number of molecules in the sample, n_L of which are left-handed ($3G' > 0$) and n_R of which are right-handed ($3G' < 0$): passing $N = N_L + N_R < n$ molecules from this sample through a discriminatory chiral diffraction grating and counting the numbers N_L and N_R that appear to the left and right of the line of zero angular deflection in the resulting diffraction pattern would allow ee to be inferred from the fractional difference $\Delta = (N_L - N_R)/(N_L + N_R)$, the variation of which with ee and E_0^2 for hexahelicene is seen in figure 5.17. A particularly appealing feature of Δ is that it can in principle be determined using detectors of low spatial resolution, as N_L and N_R are the only quantities that need to be measured. This is in line with recent molecular diffraction experiments centred upon the dipole potential energy, where simple measurements of total molecule flux, with no spatial resolution, have found favour [208–210, 222].

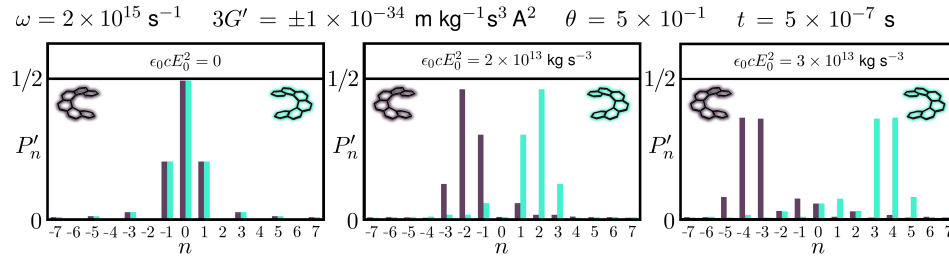


Figure 5.16: Plots of the modified diffraction probabilities P'_n , depicting their variation with the notional intensity $\epsilon_0 c E_0^2$ for hexahelicene.

It is possible, of course, to conceive of other novel possibilities offered for chiral molecules in the regime of de Broglie molecular optics by the discriminatory potential energy. We will return to these ideas elsewhere.

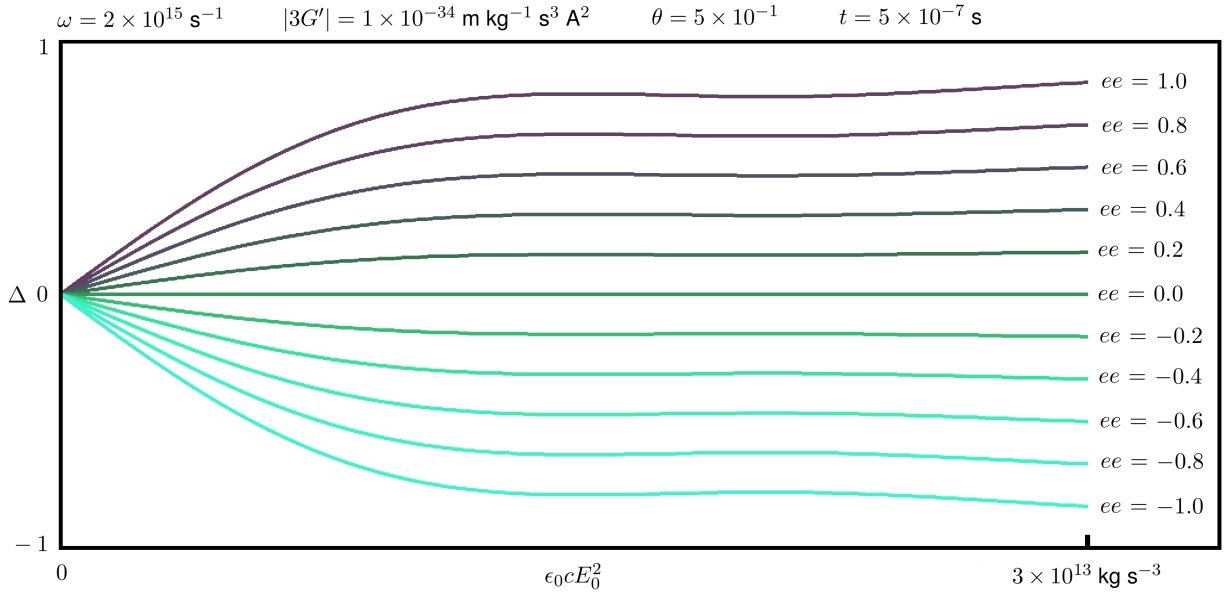


Figure 5.17: The enantiomeric excess ee of a sample of chiral molecules could be measured, simply and to high precision, by passing some of these molecules through a discriminatory chiral diffraction grating and measuring the fractional difference Δ exhibited by the resulting diffraction pattern.

Thus concludes our present discussion of the discriminatory optical force. It should be noted that molecular polarisabilities, upon which our approach is based, are state dependent [25]. This may give rise to interesting subtleties and additional possibilities for manipulation. We have imagined the molecule to be tumbling freely in the optical field, thus neglecting the possibility of alignment effects and treating the molecule, heuristically, in an isotropic manner. In reality, the molecule might initially occupy a suitable thermal mixed state of ‘high’ temperature that spans many rotational levels, for example. At ‘low’ temperatures and / or ‘high’ optical intensities, however, polarisation-dependent alignment effects in certain optical fields may be important [211, 212], giving rise to further subtleties and possibilities for manipulation. It remains to further ascertain the feasibility of our proposed devices for realistic beams of light rather than plane waves. These are tasks for future research.

5.5 Discussion

We have examined a well established manifestation of optical activity (optical rotation §5.2), a dormant manifestation of optical activity (differential scattering; §5.3) and a new manifestation of optical activity (discriminatory optical force for chiral molecules; §5.4). Underpinning our investigations was our observation that these phenomena can be related explicitly to helicity, spin, the *ab* infra zilches etc. We should note, however, that such relations do not appear to be of *fundamental* significance. As we have worked exclusively with monochromatic light we could have instead identified the zilch or any other of the lower- and higher-order extensions of helicity, spin, the *ab* infra zilches etc, following our observations in §3.4. Moreover, had we extended our calculations beyond the e^2 regime, we would have met, ultimately, with non-linear terms which cannot obviously be related to any conserved properties of freely propagating light, as the latter are bilinear. Nevertheless, the identification of optical activity phenomena with the angular momentum of light where possible is certainly interesting and indeed, has led us to new insights, if only in a pragmatic sense. There remains much to be explored, of course: possible avenues for future research are highlighted in §6.

Chapter 6

Future Research

I have recognised an abundance of new possibilities pertaining to chirality and optical activity following on from the research presented in §5. For example

- The effects of the discriminatory optical force can be amplified, it seems, using certain types of polychromatic light. This would serve to greatly extend the domain of applicability of my proposed devices.
- The discriminatory optical force can form the basis of molecular and atomic interferometers with which to probe the fascinating left-right asymmetry inherent to the (electro)weak interaction itself, which manifests itself subtly in molecules and atoms. Information obtainable through molecular and atomic parity violation experiments can complement that afforded by large-scale particle accelerators and advance our understanding of fundamental physics [28].
- New devices based upon the discriminatory optical force might enable molecular lithography and deposition at the nanoscale with a chiral twist, allowing in turn for the fabrication of chiral metamaterials that exhibit negative refraction for visible light: chiral molecules are, of course, the smallest possible chiral building blocks. Such materials afford remarkable possibilities, for example the ability to image objects smaller than is permitted by conventional optics and the construction of invisibility cloaks [232].
- The translational cooling of molecules is still in its infancy [233], however the discriminatory optical force could one day form the basis of structured light in which to distil and investigate enigmatic new states of matter comprised of chiral molecules, analogous to the current use of the dipole optical force to distil and investigate various arrangements of atoms in optical lattices [177]. This would allow for incisive studies of the role played by chirality in molecular collisions and chemical reactions.
- Manifestations of optical activity associated purely with rotational dynamics afford the possibility of gaining new information about the overall structures of molecules. Although they have been considered in a small body of theoretical work concerned with the extension of well-established optical activity methods into the microwave domain [234], no experimental observations have been reported to date [25]. The obstacle is the unfavourable scaling of conventional optical activity phenomena with frequency. In spite of the fact that it is not obviously a

manifestation of optical activity, the recently demonstrated use of pure rotational transitions to probe the chirality of molecules through nonlinear interactions with microwaves [148, 149] has revealed to me a concrete means by which to proceed.

- Entirely new information about the structures of molecules and atoms is afforded by optical activity induced in Raman scattering by a static electric field. Indeed, manifestations of electric optical activity are rare: electric analogues of magnetic optical rotation and magnetic circular dichroism, for example, do not exist. In spite of its allure, electric Raman optical activity has not been observed in experiment or studied quantitatively in theory [163] and I hope to rectify this.
- Optical activity in the emission of light yields information about the excited states of molecules and atoms rather than their ground states as in circular dichroism [25, 143]. I am interested in the as yet unexplored possibility of enhancing the phenomenon by engineering the environments in which the molecules and atoms reside so as to see it better utilised.
- An enantiomeric molecular switch is a molecule that can be interconverted between left- and right-handed forms by circularly polarised light [235]. Such switches have been employed as dopants in (otherwise achiral) nematic liquid crystals, where they are found to induce a strongly chiral nematic phase which can then be controlled optically [236]. Molecular switches could also be used one day in computers as minute memory elements. I have observed in a preliminary study that enantiomeric molecular switches can be sensitive to the angular momentum of light. Thus, they might form the basis of novel optical angular momentum sensors, either by themselves or as dopants in liquid crystals. Conversely, the angular momentum of light might be used to selectively address chiral molecular switches or to manipulate the chirality of liquid crystals, for example.

The Engineering and Physical Sciences Research Council have awarded me a Postdoctoral Fellowship to pursue these ideas further. Wish me luck!

THE END

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